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Composite structure and method for producing the composite structure

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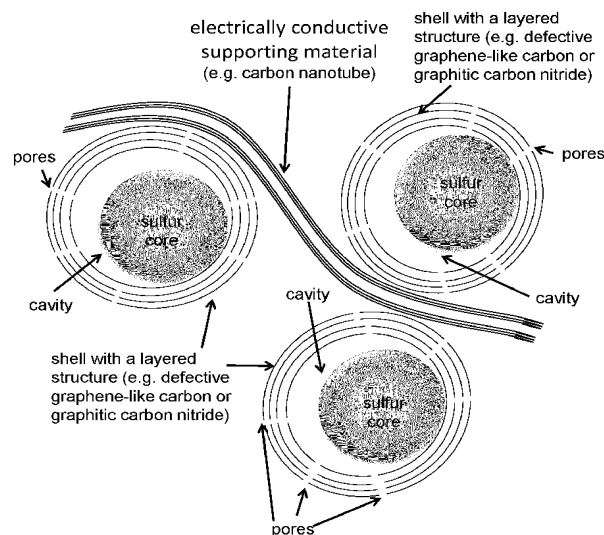
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Fig. 1



(57) Abstract: A composite structure for an electrode, comprising: a conductive supporting material a plurality of core-shell structures, said core-shell structures comprising: a shell comprising carbon, a cavity enclosed by the shell, a core in the cavity, said core comprising sulfur, wherein the shell has a layered structure and comprises pores connecting the cavity and outside of the shell, said pores have an average thickness ranging from 0.2nm to 5nm, preferably from 0.4 to 2nm, more preferably from 0.4 to nm, wherein the plurality of core-shell structures are dispersed in the composite structure by the conductive supporting material between the plurality of core-shell structures.

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Composite structure and method for producing the composite structure

Field of the invention

- 5 **[0001]** The invention relates to a composite structure and a method for producing the composite structure.

Background of the invention

- 10 **[0002]** Metal-sulfur batteries comprise lithium-sulfur (Li-S) batteries, sodium-sulfur (Na-S) batteries, magnesium-sulfur (Mg-S) batteries, aluminum-sulfur (Al-S) batteries, potassium-sulfur (K-S) batteries, calcium-sulfur (Ca-S) batteries, zinc-sulfur (Zn-S) batteries, iron-sulfur (Fe-S) batteries, Barium-sulfur (Ba-S) batteries, Chromium-sulfur (Cr-S) batteries, and so forth. In common, the metal-based electrodes work as the
- 15 anodes (negative electrodes) and sulfur-based electrodes serve as cathodes (positive electrodes). Metal-sulfur batteries own high gravimetric and volumetric energy densities and low cost, which are promising in future electrochemical energy storages. For example, as a typical type of metal-sulfur batteries, lithium-sulfur batteries exhibit a specific energy density as high as 2600 Wh/kg, which are ~6-8 folds of the
- 20 conventional Li-ion batteries. The volumetric energy density is around 2800 Wh/L, which is 2-3 times of the conventional Li-ion batteries. However, there are many problems hindering the commercialization of Li-S cells, including electrically and ionically insulating nature of sulfur and the discharge product sulfides, dissolution of polysulfides (S_8^{2-} , S_7^{2-} , S_6^{2-} , S_5^{2-} , S_4^{2-}) in the electrolyte, diffusion of polysulfides
- 25 between cathodes and anodes, volume expansion of sulfur cathodes during discharge and charge, slow kinetic reaction during transformation between polysulfide to sulfides ($Li_2S_4 \rightarrow Li_2S$), lithium dendrites formation on surface of lithium anodes, corrosive damage of lithium anodes, repeated generation of solid electrolyte interphase on anodes and safety issues as well. Other types of metal-sulfur batteries such as Na-S
- 30 batteries, Mg-S batteries, Al-S batteries, K-S batteries, Ca-S batteries suffer from similar problems due to the electrically and ionically insulating nature of sulfur, diffusion and migration of polysulfides and slow kinetics of electrochemical reactions. Encapsulation of sulfur and polysulfides by host materials is a common strategy to overcome these issues. However, the utilization and specific capacity of sulfur, energy
- 35 densities, power densities, and discharge-charge cyclic performances are still need to be improved due to the relatively large size of sulfur and host materials, serious

aggregation of host materials encapsulating sulfur and the abovementioned intrinsic properties of sulfur and polysulfides. Thus it is desired to solve these problems by rational design and synthesis of sulfur-based electrodes and the host materials.

5 ***Summary of the invention***

[0003] According to a first aspect, the invention provides a composite structure, which can be suitable for an electrode, the structure comprising: an electrically conductive supporting material, a plurality of core-shell structures, said core-shell structures
10 comprising, a shell comprising carbon, a cavity enclosed by the shell, a core in the cavity, said core comprising sulfur. Wherein the shell comprises a layered structure, said the layered structure comprises at least one of graphene, graphene-like carbon and graphitic carbon nitride. Wherein the shell comprises pores connecting the cavity and outside of the shell, said pores have an average size ranging from 0.2 nm to 5
15 nm, preferably from 0.4 nm to 2 nm, more preferably from 0.4 nm to 1 nm. Wherein the plurality of core-shell structures are dispersed in the composite structure by the electrically conductive supporting material between the plurality of core-shell structures to prevent the aggregation of the plurality of core-shell structures.

[0004] In an embodiment, the carbon weight percentage in the shell can be in the
20 range of 30 – 100%, preferably in the range of 39 – 100%, more preferably in the range of 80 – 100%. In an embodiment, the shell can be pure carbon. In an embodiment, the shell comprises a layered structure that may be graphene-like carbon or graphitic carbon nitride. In another embodiment, the layer-structured shell contains pores, said pores can be induced by the structural defects in the layers of
25 graphene-like carbon or graphite-like carbon nitride, and said pores can be also the intrinsic in-plane holes of carbon-nitrogen rings in the graphite-like carbon nitride layer.

[0005] In another embodiment, the structural defects can be at least one of the following types of defects: vacancy defects caused by missing at least one or more
30 carbon atoms in a carbon hexagon ring of graphene or one or more carbon and nitrogen atoms in the triazine or tri-s-triazine/heptazine rings of graphitic carbon nitride, Stone-Wales defects that are the adjacent pairs of pentagonal and heptagonal rings of graphene caused by the rotation of a single pair of carbon atoms, line defects caused by the grain boundaries between different crystallographic orientations of
35 graphene during the randomness of growth, doped graphene and graphitic carbon nitride crystals with foreign adatoms including at least one of nitrogen, oxygen, sulfur,

phosphorus, boron, hydrogen, fluorine, selenium, silicon, nickel, iron, copper, zinc, titanium, vanadium, chromium, manganese, cobalt, aluminium, germanium, zirconium, niobium, yttrium, molybdenum, lanthanum, tantalum, hafnium, tungsten, platinum, tin, cadmium, palladium, calcium, magnesium, sodium, potassium, rhodium, ruthenium, silver, gold, technetium, tellurium, iodine, arsenic, antimony, lead, cerium, europium, beryllium, bromine.

[0006] In an embodiment, the sulfur weight percentage in the core can be in the range of 70 – 100%, preferably in the range of 90 – 100%.

[0007] In an embodiment, the composite structure of the plurality of core-shell structures are dispersed by the electrically conductive supporting material with an average separation distance between the plurality of core-shell structures ranging from 0.5 nm to 150 nm, preferably from 0.7 to 50 nm, more preferably from 1 nm to 10 nm.

[0008] In another embodiment, the composite structure of the plurality of core-shell structures, wherein the electrically conductive supporting material comprises at least one of the following for reducing aggregation of the core-shell structures: carbon nanotubes, graphene, thin graphite, carbon nanofibers, reduced graphene oxides, graphene oxides, activated carbon, porous graphene, porous carbon, porous metals, porous conductive polymers.

[0009] In another embodiment, the composite structure of the plurality of core-shell structures, wherein the cavity has an average size ranging from 1 nm to 30 nm, preferably from 1 nm to 20 nm, more preferably from 1 nm to 10 nm, wherein the shell has an average wall thickness ranging from 0.4 nm to 10 nm, preferably from 0.4 nm to 3.5 nm, more preferably from 0.4 nm to 2 nm.

[0010] In another embodiment, the composite structure of one of the plurality of core-shell structures, wherein the cavity enclosed by the shell comprises an average pore volume ranging from 1.0 to 25.0 cm³/g, and the composite structure comprises an average specific surface area ranging from 200 to 3500 m²/g.

[0011] In another embodiment, the composite structure of the plurality of core-shell structures, wherein the core-shell structures comprise a sulfur content ranging from 50 to 98 wt.%; wherein the core-shell structures comprise an average area loading of sulfur ranging from 0.5 to 200 mg/cm², preferably from 0.5 to 100 mg/cm².

[0012] In another embodiment, the composite structure of the plurality of core-shell structures, wherein the shell can be functionalized at an internal surface of the shell with at least one of the following: oxygen contained functional group, nitrogen contained functional group, sulfur contained functional group, boron contained

functional group, halogen contained functional group, said functional groups are used for trapping soluble and polar polysulfides and lowering activation barrier energy of oxidation of Li_2S and other non-lithium metal sulfides.

5 [0013] In another embodiment, the composite structure of the plurality of core-shell structures, wherein the shell encloses catalyst nanoparticles, such as metal, metal oxides, metal nitrites, metal sulfides, metal carbides, metal hydroxides, alloys, said catalyst nanoparticles are used for trapping soluble and polar polysulfides and lowering activation barrier energy of oxidation of Li_2S and other non-lithium metal sulfides.

10 [0014] In another embodiment, an electrode comprising the composite structure of the plurality of core-shell structures.

[0015] In another embodiment, a current collector of an electrode for a metal-sulfur battery containing the composite structure of the plurality of core-shell structures.

15 In another embodiment, a method for producing a composite structure, wherein said structure can be suitable for use in an electrode of the metal-sulfur batteries, the method comprising the steps of: dissolving carbon-based organics in a colloid of at least one of metal, metal hydroxides and metal oxide nanoparticles, and adding a conductive supporting material to form a mixed colloid; drying the mixed colloid to obtain a composite of solid-carbon wrapped at least one of metal, metal hydroxides
20 and metal oxide nanoparticles, said composite dispersed by the conductive supporting material; heat-treating the obtained composite at a temperature from 200 °C to 900 °C under inert gas protection to obtain graphene-like carbon coated at least one of metal nanoparticles and metal oxides nanoparticles by catalytic conversion of the solid-carbon to graphene-like carbon or growth of graphitic carbon nitride; removing
25 one of metal and oxide nanoparticles to obtain a plurality of shell structures, said plurality of shell structures are dispersed by the conductive supporting material, said shell structures comprise: a shell comprising carbon, a cavity enclosed by the shell, wherein the shell comprises pores connecting the cavity and outside of the shell, said shell comprises a layered structure made up of one of graphene-like carbon and graphitic carbon nitride, said pores have an average size ranging from 0.2 nm to 5
30 nm, preferably from 0.4 nm to 2 nm, more preferably from 0.4 nm to 1 nm; encapsulating sulfur in the cavities as cores enclosed by the shells to obtain the composite structure, said cores comprising sulfur.

35 [0016] In another embodiment, the method for producing a composite structure comprising the shell of graphene-like carbon for an electrode, wherein the metal hydroxides and metal oxides nanoparticles may be at least one of transition metal

oxides, transition metal hydroxides, magnesium hydroxides, magnesium oxide, aluminium hydroxides, aluminium oxides, calcium hydroxide, calcium oxide, and a combination of two or more from the list, said nanoparticles can be non-porous structure.

5 [0017] In another embodiment, the method for producing a composite structure comprising the shell of graphitic carbon nitride for an electrode, wherein the metal hydroxides and metal oxides nanoparticles may be at least one of transition metal oxides, transition metal hydroxides, magnesium hydroxides, magnesium oxide, aluminium hydroxides, aluminium oxides, calcium hydroxide, calcium oxide, and a
10 combination of two or more from the list, said nanoparticles can be non-porous structure.

[0018] In another embodiment, the method for producing a composite structure for an electrode, wherein the carbon-based organics or/and the solid carbon comprises at least one of polyvinylpyrrolidone, hydrocarbon, sugar, sucrose, polyvinyl alcohol,
15 polyethylene oxide (PEO), polyoxyethylene, poly(methyl methacrylate), triethylene glycol, lignin, dicyandiamide, melamine, urea, proteins, nylon, rubber.

[0019] In another embodiment, the method for producing a composite structure for an electrode, further comprising synthesizing sulfur in the cavity by placing the plurality of shell structures with the supporting material in liquid sulfur at a temperature ranging
20 from 100 to 600 °C under an atmosphere comprising at least one of Argon and Nitrogen.

[0020] In another embodiment, the method for producing a composite structure for an electrode, further comprising functionalising by surface chemical modifications such as oxidation, reaction with oxygen/nitrogen/sulfur/boron/halogen contained functional
25 groups at an internal surface of the shell with at least one of the following: oxygen contained functional group, nitrogen contained functional group, sulfur contained functional group, boron contained functional group, halogen contained functional group, for trapping soluble and polar polysulfides and lowering activation barrier energy of Li₂S and other non-lithium metal sulfides.

30 [0021] In another embodiment, the method for producing a composite structure for an electrode, further comprising enclosing catalyst nanoparticles, such as metal, metal oxides, metal nitrites, metal sulfides, metal carbides, metal hydroxides, alloys, for trapping soluble and polar polysulfides and lowering activation barrier energy of Li₂S and other non-lithium metal sulfides.

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Brief description of the Figures

[0022] Embodiments of the present invention will be described hereinafter, by way of example only, with reference to the accompanying drawings which are schematic in nature and therefore not necessarily drawn to scale. Furthermore, like reference signs in the drawings relate to like elements.

[0023] Figure 1-3 are schematic, cross-sectional view of examples of a method for making the composite structure disclosed herein;

[0024] Figure 4 shows a schematic illustration of the synthesis of fullerenes or carbon onions-sulfur composites anchored on carbon nanotube (CNT) networks in the assistance of Ni nanoparticles (NPs) and used for lithium-sulfur batteries according to an embodiment of the invention.

[0025] Figure 5a shows an HRTEM image of $\text{Ni}(\text{OH})_2$ nanoparticles.

[0026] Figure 5b shows a SEM image of fullerene@Ni NPs.

[0027] Figure 5c shows a TEM image of fullerene@Ni NPs.

[0028] Figure 5d shows an HRTEM image of fullerene@Ni NPs.

[0029] Figure 5e shows a TEM image of fullerene-like carbon.

[0030] Figure 5f shows an HRTEM image of fullerene-like carbon.

[0031] Figure 6a shows an HRTEM image of fullerene@CNT composites.

[0032] Figure 6b shows an HRTEM image of the CNT.

[0033] Figure 6c shows an opening of CNT according to an embodiment of the invention.

[0034] Figure 6d shows an HRTEM image of a monolayer fullerene sphere (marked with white arrow) anchored on CNT.

[0035] Figure 6e shows an HRTEM image of multilayer fullerene spheres (marked with orange arrows) anchored on CNT.

[0036] Figure 7a shows a TEM image of fullerene@S NPs@CNT.

[0037] Figure 7b shows an HRTEM image of fullerene@S NPs@CNT.

[0038] Figure 7c shows an HRTEM image of fullerene@S NPs@CNT

[0039] Figure 7d shows an HRTEM image of sulfur encapsulated in tubular cavities of CNT.

[0040] Figure 8a shows the cycling performances of fullerene@S NPs@CNT at 0.2 C (334 mA/g) and a physical mixture of fullerene@S NPs with CNT.

[0041] Figure 8b shows the cycling performances of fullerene@S NPs@CNT at 5 C (8.35 A/g).

[0042] Figure 9 shows a schematic illustration of the charge and discharge processes of fullerene@S NPs@CNT according to an embodiment of the invention.

[0043] Figure 10a and b show the fullerenes or carbon nanotubes embed with CeO₂ nanoparticles.

Detailed description

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[0044] Metal-sulfur batteries including Li-S batteries, Na-S batteries, Mg-S batteries, Al-S batteries, K-S batteries, Ca-S batteries, Zn-S batteries, Fe-S batteries, Ba-S batteries, Cr-S batteries have high energy densities and relatively low costs. Metal-sulfur batteries are promising in the applications of future electrochemical energy storages for portable electronics such as computers, mobile phones, and also for electrical grids and electrical transportations such as electrical vehicles. In the metal-sulfur batteries, the metal-based electrodes work as the anodes (negative electrodes), while the sulfur-based electrodes serve as the cathodes (positive electrodes). However, the metal-sulfur batteries suffer from rapid capacity decay and low capacities that hamper their commercialization mainly due to the common issues from sulfur cathodes, polysulfides species and slow kinetics of electrochemical reactions.

[0045] More specifically, the sulfur cathodes of lithium-sulfur batteries have highly poor electrical and ionic conductivity of both sulfur and lithium sulfide (end product after fully discharge);

[0046] The intermediates of polysulfides (Li₂S_x, x=3-8) formed during the discharge can dissolve in the electrolyte and cause low capacity and fast decay during cycling.

[0047] The intermediate polysulfides formed during the discharge have “shuttle phenomenon” that the polysulfides can pass through the separator, deposit onto lithium anodes, corrode lithium and then result in the fast capacity decay.

[0048] The diffusion lengths of lithium ions in sulfur/carbon particles are too long, which influences the rate performances and the utilization of sulfur.

[0049] The phase transformation between long-chain polysulfides and lithium sulfide (Li₂S₄↔Li₂S₂↔Li₂S) is a slow liquid-to-solid reaction in kinetics, which reduces the rate performances of Li-S cells.

[0050] There is a volume expansion of electrodes during discharge because of the different densities of sulfur and lithium sulfide.

[0051] The Al current collectors are heavy and not stable comparing with carbon materials. The Al current collectors can reduce the gravimetric/volumetric capacities of sulfur electrodes.

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[0052] These technical problems have been partly addressed in various ways in previous studies. For example, various kinds of conductive additives or porous materials were introduced to improve the electric conductivity of sulfur cathodes, for example carbon black, graphite, activated carbon, carbon nanotube, graphene, porous carbon and graphene, metals oxides, metal sulfides, metals, conductive polymers etc. Although the conductivities of sulfur and lithium sulfide are increased, but the contact between sulfur and carbon is still needed to be improved.

[0053] A method for solving the electrically and ionically insulating nature problems of sulfur cathodes and trapping polysulfide ions is by encapsulation of sulfur in a conductive matrix, which comprises metals, carbons, polymers and so forth. Due to the good chemical stability, high electric conductivity and light weight, carbonaceous matrixes are those of the most attractive ones. These carbonaceous matrixes including graphite, carbon black, ketjen black, activated carbon, ordered mesoporous carbon, hollow carbon spheres, carbon nanotubes, carbon nanofibers, graphene, fullerene, their mixtures and the like. Normally two types of encapsulation of sulfur in carbon matrix includes (i) filling sulfur in the micropores, mesopores and macropores of carbon, and (ii) cover sulfur particles with carbon materials such as graphene layers, carbon black particles, carbon nanotube, and polymers. Through the composite structure and physical confinements, the electric conductivity of sulfur can increase. The polysulfide species formed during discharge and charge can be largely trapped in the carbonaceous materials, instead of dissolving in electrolyte and diffusing to the anode sides.

[0054] In the carbon-sulfur composites, the pore sizes of carbon matrix have been decreased from macroporous to mesoporous and microporous, meanwhile the sulfur filled in the pores also decreased from tens microns to few nanometers. However, the particle size of sulfur-conductive matrix composites can be rather big. For example, the particle sizes of S-C composites can be from 50 nm to several or tens microns. The large particle size could increase the electric resistivity of S-C composites and diffusion length for ions, and reduce the diffusivity of lithium/non-lithium metallic cations. As a result, the electrodes with large particle sizes of S-C composites exhibit much lower specific capacity than the theoretical specific capacity of sulfur (1675 mAh/g) and poor cyclic performances. By decreasing the particle size of sulfur from hundreds nanometer to dozens or even few nanometers, the utilization of sulfur can be dramatically increased. However, the sulfur nanoparticles are exposed to electrolyte and the polysulfides are still dissolved fast. Encapsulation of sulfur nanoparticles with sub-dozens nanometers into individual nanometer-sized cavities

enclosed by carbon-based shell can be a rational design to achieve the high specific capacity of sulfur and good cyclic stability. Thus, inventing nanometer-sized carbon-based hollow spheres for encapsulation of sulfur inside the cavity and for S-C composites of very small S-C particle sizes is very promising and crucial for achieving high-capacity, high-rate and long-term lifespan lithium-sulfur batteries and other non-lithium metal-sulfur batteries. Nonetheless, in most cases small nanoparticles usually tend to aggregate together and form large aggregates during synthesis. As a consequence, the contact between the nanoparticles of the aggregates and the electrolyte of batteries may be significantly reduced. Anti-aggregation of small S-C particles is thus extremely important and crucial for developing high-performance lithium-sulfur batteries and non-lithium metal-sulfur batteries. Therefore, introducing an electrically conductive supporting material during the synthesis of small S-C particles not only can facilitate the transport of electrons but also can reduce the aggregation of small S-C particles.

[0055] Different types of encapsulation of sulfur in carbon and polymer have been reported in previous works. Zhou et al. (US 2015/221935 A1) describes a core-shell structure for sulfur cathodes of Li-S batteries in which a sulfur core is enclosed by a porous carbon shell. The method for synthesis of porous carbon shell is by using porous templates such as mesoporous silica. Carbon precursors are then deposited on the surface and into the pores of porous templates. In following, the mixture is pyrolyzed below 1000 °C, the porous carbon shell and the hollow core are obtained after removal of the porous templates. After that, an additional polymer coating on the carbon shells is synthesized by polymerization. The shell is indeed an amorphous carbon and created by removal of the porous templates. The pore size of the shell is 1-20 nm and the hollow core is in sub-micron. Sub-micron sulfur particles encapsulated by the porous carbon shell are still too large to be fully utilized for cathode. The relative low diffusivity of lithium ions and long diffusion length also limit the rate performances of the batteries. For example, Zhou et al. obtained a much lower specific capacity (the highest initial specific capacity 1141 mAh/g) than the theoretical specific capacity of sulfur (1675 mAh/g). In addition, Zhou et al. does not disclose and suggest neither a sub-tens nanometers cavity enclosed by a layered shell of graphene-like carbon or graphitic carbon nitride, nor a layered shell comprising sub-nm pores. Zhou et al. also does not disclose and suggest the anti-aggregation method during synthesis of small C-S nanoparticles.

[0056] Wang et al. develops a hierarchical nanostructure of meso-C coated MWCNT (multi-walled carbon nanotubes) as host material for sulfur cathodes of Li-S batteries

(Wang et al., Infiltrating sulfur in hierarchical architecture MWCNT@meso C core-shell nanocomposites for lithium-sulfur batteries, Phys. Chem. Chem. Phys., 2013, 15, 9051-9057). In the nanostructure the electrically conductive MWCNT is the core and meso-C coating is the porous shell. The architecture has a one dimensional structure. After infiltration with sulfur, sulfur distributed in the meso-C shell. However, the sulfur particles are not encapsulated but exposed directly to the electrolyte of batteries, leading to fast capacity decay and much lower specific capacity than the theoretical specific capacity of sulphur. A core-shell structure with a sub-dozens nanometer-sized core and layered shell with sub-nanometer pores are neither disclosed nor suggested in this reference.

[0057] Muldoon et al. (US 2016/0087266 A1) describes a core-shell sub-micron particle, which contains a sub-micron sulfur core enclosed by a first shell of an ionically charged conductive copolymer and a second conductive polymer layer. The functionalized carbon black added to improve the conductivity is optionally dispersed inside the sulfur core and on or embedded in an outermost conductive polymer layer. The sub-micron sulfur particles are formed by precipitation from solution. In fact, the sub-micron sulfur particles are still too large to achieve a close-to-theoretical specific capacity and good rate performances. A core-shell structure with a sub-dozens nanometer core and layered shell with sub-nm pores are neither disclosed nor suggested in this reference.

[0058] In addition to the encapsulation strategy, another way to reduce the dissolution and diffusion of polysulfides is by surface chemical interactions by using some organic and inorganic materials. Surface functionality, intrinsic polarity, and electro-/nucleophilicity can be employed to trap soluble and polar polysulfides on the electrochemical active sites. Some of the functional surfaces can also lower the activation barrier energy of oxidation of metal sulfides, accelerating the rate performances and high-rate cycling performances. Metal oxides, sulfides, carbides, nitrides, phosphides and chemical functional groups including those containing oxygen, nitrogen, sulfur, fluorine, chlorine, and bromine atoms have positive effects on trapping polysulfides. A good host material for sulfur together with synergetic effect via the surface functionality using some organic and inorganic materials can be more promising for solving the issues from sulfur and polysulfides in metal-sulfur batteries.

[0059] Furthermore, to prevent the "shuttle effect" of polysulfides, various kinds of interlayers and modification of separators were developed. The interlayer includes carbon nanotube, Super P carbon black, graphene (oxides), porous graphene, metal oxides, metal organic frameworks, and their mixtures. Lithiated Nafion, PEO, Li-PFSD

(lithium perfluorinated sulfonyl dicyanomethide), PAH [poly(allylamine hydrochloride)] and PAA [poly(acrylic acid)] etc. modified separators have effective improvements in the performances of lithium-sulfur batteries. The use of interlayer cannot fully solve the low utilization of sulfur and dissolution and diffusion of polysulfides. It can also increase the weight of the cells because of the thick interlayers used.

[0060] The present invention provides a novel composite structure of sulfur cathodes for metal-sulfur (Me-S) batteries such as lithium-sulfur (Li-S) batteries. The novel composite structure comprises an electrically conductive supporting material and a plurality of core-shell structures. The core-shell structures comprise a layered carbon-based shell and a small cavity enclosed by the shell, while a small core comprises small nanoparticles in the cavity. The size of the cavity is smaller than 30 nm, preferably from 1 nm to 20 nm, more preferably from 1 nm to 10 nm. The shell comprises a layered structure consisted of graphene-like carbon or graphitic carbon nitride. The shell has a thickness from 0.34 nm to 5 nm, preferably from 0.68 nm to 2 nm, more preferably from 1 nm to 2 nm. On the shell there are pores that connect the cavity and outside of the shell. The pores on the shell have an average size ranging from 0.2 nm to 5 nm, preferably from 0.4 nm to 2 nm, more preferably from 0.4 nm to 1 nm. The core-shell structures are uniformly dispersed in the composite structure by the conductive supporting material between the core-shell structures that reduce the aggregation of core-shell structures.

[0061] The shell of the core-shell structures may contain defects that can be at least one of the following types of defects: vacancy defects caused by missing at least one or more carbon atoms in a carbon hexagon ring of graphene or one or more carbon and nitrogen atoms in the triazine or tri-s-triazine/heptazine rings of graphitic carbon nitride, Stone-Wales defects that are the adjacent pairs of pentagonal and heptagonal rings of graphene caused by the rotation of a single pair of carbon atoms, line defects caused by the grain boundaries between different crystallographic orientations of graphene during the randomness of growth, doped graphene and graphitic carbon nitride crystals by foreign adatoms including at least one of nitrogen, oxygen, sulfur, phosphorus, boron, hydrogen, fluorine, selenium, silicon, nickel, iron, copper, zinc, titanium, vanadium, chromium, manganese, cobalt, aluminium, germanium, zirconium, niobium, yttrium, molybdenum, lanthanum, tantalum, hafnium, tungsten, platinum, tin, cadmium, palladium, calcium, magnesium, sodium, potassium, rhodium, ruthenium, silver, gold, technetium, tellurium, iodine, arsenic, antimony, lead, cerium, europium, beryllium, bromine.

[0062] In addition, on the basis of the core-shell structure, catalysts nanoparticles for metal-sulfur batteries can be also embedded into the cavities enclosed by the shell. The catalysts nanoparticles can further trap polysulfides, promote the conversion between sulfur and metal sulfides, including the conversion between polysulfides, sulfur and metal sulfide. These catalysts nanoparticles include at least one of metal, metal oxide, metal nitride, metal carbide, metal sulfide, metal phosphide, metal hydroxide, metal selenide, metal telluride, metal boride and the heterostructures of two or more listed above. The metal of the metal nanoparticles and metallic compounds nanoparticles as the catalysts can be lithium, nickel, iron, copper, zinc, titanium, vanadium, chromium, manganese, cobalt, zirconium, niobium, yttrium, molybdenum, lanthanum, tantalum, hafnium, tungsten, platinum, cadmium, palladium, rhodium, ruthenium, technetium, tellurium, lead, tin, silver, gold, magnesium, calcium, sodium, potassium, cerium, europium, beryllium and the combination of two or more of them. With using the catalysts imbedded in the core-shell structure used for the metal-S batteries, the cyclic stability, reversible capacities, energy densities and power densities can be improved.

[0063] In addition, the internal or external surfaces of the shell can be optionally tuned by surface functionalization with organic/inorganic materials, which could be oxygen contained functional groups such as hydroxyl, carbonyl, aldehyde, haloformyl, carbonate ester, carboxylate, carboxyl, ester, methoxy, or nitrogen contained functional groups such as amide, amines, imine, nitrile, isonitrile, pyridyl, or sulfur contained functional groups such as sulfhydryl, sulfide, sulfinyl, or boron contained functional groups, or halogen contained functional groups. These functional groups can trap soluble and polar polysulfides and lower the activation barrier energy oxidation of Li_2S and other non-lithium metal sulfides. Through surface functionalization with the abovementioned functional groups on the internal or external surfaces of the shell used for the metal-S batteries, the cyclic stability, reversible capacities, energy densities and power densities can be improved.

[0064] Promisingly, the metal-sulfur batteries comprising the composite structure are but not limit to lithium-sulfur (Li-S) batteries, sodium-sulfur (Na-S) batteries, magnesium-sulfur (Mg-S) batteries, aluminum-sulfur (Al-S) batteries, potassium-sulfur (K-S) batteries, calcium-sulfur (Ca-S) batteries, zinc-sulfur (Zn-S) batteries, iron-sulfur (Fe-S) batteries, barium-sulfur (Ba-S) batteries, chromium-sulfur (Cr-S) batteries, and so forth.

[0065] One example of the as-disclosed composite structure is the fullerene-sulfur core-shell particles anchored on carbon nanotubes (CNT) for metal-sulfur (Me-S)

batteries such as lithium-sulfur (Li-S) batteries. In the fullerene-sulfur core-shell particles of the composite structure, sulfur nanoparticles are encapsulated in the cavities of fullerenes (also named as carbon nanoonions), which is different from the previously disclosed structures. The shell is graphene-like carbon and has layered structure of graphene. The size of the cavity is smaller than 30 nm, preferably from 1 nm to 20 nm, more preferably from 1 nm to 10 nm. The shell has a thickness from 0.34 nm to 5 nm, preferably from 0.68 nm to 2 nm, more preferably from 1 nm to 2 nm. On the shell there are defect-induced pores that connect the cavity and outside of the shell. The pores on the shell have an average size ranging from 0.2 nm to 5 nm, preferably from 0.4 nm to 2 nm, more preferably from 0.4 nm to 1 nm. The fullerene-sulfur core-shell structures are uniformly dispersed in the composite structure by the CNT between the fullerene-sulfur core-shell structures that reduce the aggregation of fullerene-sulfur core-shell structures.

[0066] For metal-sulfur batteries such as Li-S batteries, the fullerene-sulfur composite as cathodes exhibit very excellent performances, including high specific capacities (both based on sulfur and electrodes), long-term cycling life, good rate performances, etc. The initial specific capacity of the composites can reach the theoretical value of sulfur (1675 mAh/g). During discharge and charge, the lithium ions can diffuse and pass through the graphene walls of fullerenes because of the holes on graphene walls induced by the defects. At the same time, the defective graphene walls can prevent the diffusion and shuttling of long-chain polysulfides. Importantly, the diffusion lengths of the lithium ions in a fullerene-sulfur particle are very short during charge and discharge. To the best of our knowledge, this is the shortest diffusion lengths (below 10 nm) among the reported individual C-S particles with a structure of sulfur encapsulated in a carbon host. Owing to these unique features of our disclosed structure, the electrochemical performances are very outstanding.

[0067] The shell of the core-shell structure of the fullerene-sulfur composite can be doped with foreign adatoms on the external or internal surface of graphene-like carbon shells. The foreign adatoms includes at least one of nitrogen, oxygen, sulfur, phosphorus, boron, hydrogen, fluorine, selenium, silicon, nickel, iron, copper, zinc, titanium, vanadium, chromium, manganese, cobalt, aluminium, germanium, zirconium, niobium, yttrium, molybdenum, lanthanum, tantalum, hafnium, tungsten, platinum, tin, cadmium, palladium, calcium, magnesium, sodium, potassium, rhodium, ruthenium, silver, gold, technetium, tellurium, iodine, arsenic, antimony, lead, cerium, europium, beryllium, bromine.

[0068] In addition, on the basis of the fullerenes, catalysts for metal-sulfur batteries can be also embedded into the cavities of the fullerenes. The catalysts can further trap polysulfides and promote the conversion between sulfur and lithium sulfides, including the conversion between polysulfides, sulfur and lithium sulfide. These catalyst nanoparticles include at least one of metal, metal oxide, metal nitride, metal carbide, metal sulfide, metal phosphide, metal hydroxide, metal selenide, metal telluride, metal boride and the heterostructures of two or more listed above. The metal of the catalytic metal nanoparticles and metallic compound nanoparticles can be lithium, nickel, iron, copper, zinc, titanium, vanadium, chromium, manganese, cobalt, zirconium, niobium, yttrium, molybdenum, lanthanum, tantalum, hafnium, tungsten, platinum, cadmium, palladium, rhodium, ruthenium, technetium, tellurium, lead, tin, silver, gold, magnesium, calcium, sodium, potassium, cerium, europium, beryllium and the combination of two or more of them.

[0069] In addition, the internal or external surfaces of fullerenes (carbon nanooions) can be optionally tuned by surface functionalization with organic/inorganic materials, which could be oxygen contained functional groups such as hydroxyl, carbonyl, aldehyde, haloformyl, carbonate ester, carboxylate, carboxyl, ester, methoxy, or nitrogen contained functional groups such as amide, amines, imine, nitrile, isonitrile, pyridyl, or sulfur contained functional groups such as sulfhydryl, sulfide, sulfinyl, or boron contained functional groups, or halogen contained functional groups.

[0070] Another example of the as-disclosed composite structure is the sulfur core-shell of graphitic carbon nitride particles anchored on carbon nanotubes (CNT) for metal-sulfur (Me-S) batteries. In the core-shell structures, sulfur nanoparticles are encapsulated in the cavities enclosed by the graphitic carbon nitride ($g-C_3N_4$) shell that has one or more layers. The size of the cavity is smaller than 30 nm, preferably from 1 nm to 20 nm, more preferably from 1 nm to 10 nm. The shell has a thickness from 0.32 nm to 5 nm, preferably from 0.6 nm to 3 nm. On the shell there are pores that connect the cavity and outside of the shell. The pores on the shell have an average size ranging from 0.4 nm to 5 nm, preferably from 0.4 nm to 2 nm, more preferably from 0.4 nm to 1 nm. The S core- $g-C_3N_4$ shell structures are uniformly dispersed in the composite structure by the CNT between the core-shell structures that reduce the aggregation.

[0071] In addition, on the basis of the $g-C_3N_4$ hollow structure, catalysts for metal-sulfur batteries can be also embedded into the cavities of the $g-C_3N_4$ hollow structure.

The catalysts can further trap polysulfides and promote the conversion between sulfur and lithium sulfides, including the conversion between polysulfides, sulfur and lithium

sulfide. These catalysts nanoparticles include at least one of metal, metal oxide, metal nitride, metal carbide, metal sulfide, metal phosphide, metal hydroxide, metal selenide, metal telluride, metal boride and the heterostructures of two or more listed above. The metal of the metal nanoparticles and metallic compounds nanoparticles as the catalysts can be lithium, nickel, iron, copper, zinc, titanium, vanadium, chromium, manganese, cobalt, zirconium, niobium, yttrium, molybdenum, lanthanum, tantalum, hafnium, tungsten, platinum, cadmium, palladium, rhodium, ruthenium, technetium, tellurium, lead, tin, silver, gold, magnesium, calcium, sodium, potassium, cerium, europium, beryllium and the combination of two or more of them.

[0072] In addition, the internal or external surfaces of the g-C₃N₄ hollow structure can be optionally tuned by surface functionalization with organic/inorganic materials, which could be oxygen contained functional groups such as hydroxyl, carbonyl, aldehyde, haloformyl, carbonate ester, carboxylate, carboxyl, ester, methoxy, or nitrogen contained functional groups such as amide, amines, imine, nitrile, isonitrile, pyridyl, or sulfur contained functional groups such as sulfhydryl, sulfide, sulfinyl, or boron contained functional groups, or halogen contained functional groups.

[0073] The present invention provides a method for producing the composite structure for an electrode, comprising the steps of:

dissolving carbon-based organics in a colloid of one of metal nanoparticles, metal hydroxides and metal oxide nanoparticles, and adding an electrically conductive supporting material to form a mixed colloid;

drying the mixed colloid to obtain a composite of solid-carbon wrapped the one of metal, metal hydroxides and metal oxide nanoparticles, said composite dispersed by the conductive supporting material;

heat-treating the obtained composite at a temperature ranging from 200 °C to 900 °C under inert gas protection to obtain layered defective graphene-like carbon or graphitic carbon nitride coated metal nanoparticles by catalytic conversion of the solid-carbon to defective graphene-like carbon or graphitic carbon nitride;

removing the one of metal nanoparticles and oxide nanoparticles in acid or other etchants to obtain a plurality of shell structures, said plurality of shell structures are dispersed by the conductive supporting material, said shell structures comprise:

a shell comprising carbon;

a cavity enclosed by the shell;

wherein the shell comprises pores connecting the cavity and outside of the shell,

said shell comprise layered structure of graphene-like carbon or graphitic carbon

nitride, said pores have an average size ranging from 0.2 nm to 5nm, preferably from 0.4 nm to 2 nm, more preferably from 0.4 nm to 1 nm;

encapsulating sulfur in the cavities as cores enclosed by the shells to obtain the composite structure, said cores comprising sulfur.

5 **[0074]** In particular, the method for synthesis of the composite structure are versatile due to the following features:

[0075] (1) solid carbon used for synthesis of the composite structure can be polymers and other hydrocarbon materials such as sugar, sucrose, or sputtered carbon.

10 **[0076]** (2) The solid carbon also can contains other elements such as nitrogen, sulfur, boron, phosphorus and so forth.

[0077] (3) The metal nanoparticles can be prepared before mixing with solid carbon, or can be formed during heating with solid carbon. The precursors of metal nanoparticles can be metal oxides, metal hydroxides, metal chlorides, metal complex, metal ion coordination compounds, amorphous metal and so forth.

15 **[0078]** (4) The core-shell structures of the composite structure have cavities of 1-30 nm, shells of 0.4-10 nm thickness, tunable graphitization and defects contained.

[0079] (5) The core-shell structure of the composite structure can be doped with foreign adatoms on the external of shells or internal surface of shells by chemical approaches. The foreign adatoms are referred to the abovementioned elements. The chemical approaches involves at least one of synthesis, selective etching, chemical and electrochemical deposition, oxidation, reduction, thermal treatment, photochemical reaction, decomposition, replacement reaction, solid-state reactions, substitution, addition and elimination, complexation, etc.

20 **[0080]** (6) In addition, by chemical approaches the external or internal surface of the shells of the core-shell structure in the composite structure can be optionally surface functionalized with organic/inorganic materials, which can be oxygen contained functional groups such as hydroxyl, carbonyl, aldehyde, haloformyl, carbonate ester, carboxylate, carboxyl, ester, methoxy, or nitrogen contained functional groups such as amide, amines, imine, nitrile, isonitrile, pyridyl, or sulfur contained functional groups such as sulfhydryl, sulfide, sulfinyl, or boron contained functional groups, or halogen contained functional groups. The chemical approaches involve at least one of chemical and electrochemical synthesis, deposition, oxidation, reduction, thermal treatment, photochemical reaction, decomposition, replacement reaction, solid-state reactions, substitution, addition and elimination, complexation, etc.

30 **[0081]** (7) Except, the cavities enclosed by the shell of the core-shell structure in the composite structure may be optionally filled with catalyst nanoparticles by chemical

approaches. These catalysts nanoparticles include at least one of metal, metal oxide, metal nitride, metal carbide, metal sulfide, metal phosphide, metal hydroxide, metal selenide, metal telluride, metal boride and the heterostructures of two or more listed above. The metal of the metal nanoparticles and metallic compounds nanoparticles as the catalysts can be lithium, nickel, iron, copper, zinc, titanium, vanadium, chromium, manganese, cobalt, zirconium, niobium, yttrium, molybdenum, lanthanum, tantalum, hafnium, tungsten, platinum, cadmium, palladium, rhodium, ruthenium, technetium, tellurium, lead, tin, silver, gold, magnesium, calcium, sodium, potassium, cerium, europium, beryllium and the combination of two or more of them. The chemical approaches involves at least one of synthesis, selective etching, chemical and electrochemical deposition, oxidation, reduction, thermal treatment, photochemical reaction, decomposition, replacement reaction, solid-state reactions, substitution, addition and elimination, complexation, carburizing, nitriding, chemical vapor deposition, etc.

[0082] A novel method for synthesis of the sulfur core-fullerene shell composite and a novel design of the sulfur core-fullerene shell composites cathodes has been developed by using fullerenes (carbon nanooxions) for metal-sulfur batteries such as lithium-sulfur batteries. The new method and products of fullerene-sulfur composites according the invention have one or more of the following advantages:

[0083] The new fullerene-sulfur composite contains a core-shell structure, of which the sulfur is the core and graphene walls of fullerenes are the shell. The fullerenes have cavities of 1-30 nm, shell thickness of 0.4-10 nm. The sulfur particles encapsulated inside the cavities of fullerenes are very small (below 30 nm), and have intimate contact with graphene walls, thus the electrically conductivity of the sulfur can be significantly improved.

[0084] Thus, the new fullerene-sulfur composites have particle size of 1-30 nm, which are the smallest among the reported carbon-sulfur nanoparticles to the best our knowledge. The sulfur nanoparticles can be fully activated, which can increase the capacity of sulfur. Owing to the very small particle size of sulfur-carbon composites, the diffusion lengths of lithium ions in each S-fullerene particle are very short. So the rate performances of batteries can be significantly increased.

[0085] The graphene wall of fullerenes contains holes induced by the defects which can allow the diffusion of sulfur molecular. The holes on graphene shells also allow the diffusion of lithium ions but effectively restrict the diffusion of polysulfides formed during discharge. This can significantly prolong the service life of batteries.

[0086] The fullerene shells can effectively reduce the volume expansion of sulfur during discharge and charge.

[0087] The functionalized internal surface of fullerenes with functional groups can chemically interact with polysulfides and trap polysulfides.

5 **[0088]** The functionalized internal surface of fullerenes or embedding with catalyst nanoparticles inside of the cavities of fullerenes can significantly accelerate the kinetic of transformation between sulfur, polysulfides and lithium sulfides during discharge and charge. Thus, based on the small cavities of fullerenes, the electrochemical performances in particular such as the rate performances and service life can be
10 further enhanced synergistically by engineering the internal surface of fullerenes or embedding catalyst inside the cavities of fullerenes.

[0089] By introducing support materials such as carbon nanotube, graphite, carbon nanofibers, graphene, activated carbon, carbon cloth and so forth, the aggregation of fullerene nanoparticles can be reduced. The support materials can be also used as
15 conductive networks and current collectors. Thus, binders and aluminum current collectors may be replaced and omitted.

[0090] The other possible applications of the invention will be in energy conversion and storage, such as (non-metal-sulfur batteries, supercapacitors, oxygen reduction reaction, and hydrogen generation), catalysts and so forth.

20 **[0091]** With respect to the synthesis procedures, the graphene-like carbon shell-sulfur core composite structures are synthesized by using metal or metal oxides nanoparticles as catalysts and solid carbon as carbon precursors. First, uniformly mix one of the metal nanoparticles, metal hydroxides, metal oxides nanoparticles with carbon precursors and electrically conductive supporting materials in solution under
25 stirring and/or ultrasonication at a temperature from -30°C to 350 °C. The time mixing process can be from seconds to several days. The metal nanoparticles can be nanoparticles of transition metals such as nickel, iron, copper, zinc, titanium, vanadium, chromium, manganese, cobalt, zirconium, niobium, yttrium, molybdenum, lanthanum, tantalum, hafnium, tungsten, platinum, cadmium, palladium, rhodium,
30 ruthenium, technetium, tellurium, lead, and non-transition metals such as tin, silver, gold. The metals of metal hydroxide and oxide nanoparticles can be transition metals such as nickel, iron, copper, zinc, titanium, vanadium, chromium, manganese, cobalt, zirconium, niobium, yttrium, molybdenum, lanthanum, tantalum, hafnium, tungsten, platinum, cadmium, palladium, rhodium, ruthenium, technetium, tellurium, lead, and
35 non-transition metals such as tin, silver, magnesium, calcium, and the combination of two or more of them. Before mixing, the metal nanoparticles, metal hydroxides or

metal oxides nanoparticles can be pre-treated with acid, alkaline solution or oxidants to modify the surface of them.

[0092] The electrically conductive supporting material comprises at least one of the following: carbon nanotubes, graphene, thin graphite, carbon nanofibers, reduced graphene oxides, graphene oxides, activated carbon, porous graphene, porous carbon, porous metals, porous conductive polymers and the combination of two or more of them. The content of the electrically conductive supporting material in the composite of the graphene-like carbon hollow structure on the supporting material is from 1% to 80% by weight.

[0093] The carbon precursors in the above mixing process can be at least one of polyvinylpyrrolidone, polyvinyl alcohol, polyethylene oxide, polyoxyethylene, poly(methyl methacrylate), triethylene glycol, sugar, glucose, sucrose, lignin, dicyandiamide, melamine, urea, proteins, nylon, rubber, polyacrylonitrile, polycarbonate, polyphenylene oxide, polyurethane, polyetherimide, polyamide-imide, fructose, maltose, xylose, starch, cellulose, polyaniline, polyethylenimine, polyamide imides, carboxymethyl cellulose, polyethersulfone, and other hydrocarbon.

[0094] The solvent used in the above mixing process can be at least one of water, ethanal, toluene, butyl or amyl acetate, ethyl acetate, butanol, acetone, 2-ethoxyethanol, pyrobenzene, xylene, cyclohexanone, methyl acetate, hexane, 1,4-dioxane, chloroform, diethyl ether, dichloromethane, benzene, cyclohexane, hexane, cyclopentane, pentane, tetrahydrofuran, dimethylformamide, acetonitrile, propylene carbonate, formic acid, n-Butanol, isopropyl alcohol, n-Propanol, methanol, acetic acid, carbon disulphide, o-xylene, pyridine, methylene chloride, N-methyl-2-pyrrolidone, ethylene glycol, triethylene glycol, diethyl ether, diethylene glycol, 1,2-dimethoxy-ethane, heptane, methyl t-butyl ether, nitromethane, m-xylene, acid aqueous solution, alkaline aqueous solution, and the combination of two or more of them.

[0095] Next, dry at a temperature and pressure to obtain a composite of solid-carbon wrapped the one of metal, metal hydroxides and metal oxide nanoparticles, said composite dispersed by the conductive supporting materials. Usually, the drying temperature can be at from 0 °C to 400 °C. The pressure can be from 10^{-6} mbar to 1 bar. In addition, freeze drying, also known as lyophilisation or cryodesiccation, can be a good method for drying the mixture abovementioned. In the situation of freeze drying, the temperature can be at from -60 °C to 10 °C, meanwhile the pressure can be from 10^{-6} mbar to 1 bar. The drying time can be from few minutes to few days.

[0096] After drying, the obtained dried mixture is heat treated under protection by inert gas of at least one of argon, nitrogen. Under heat treatment at low temperatures (e.g. 200-900 °C), solid carbon is catalytically converted into layered graphene-like carbon in the assistance of metal nanoparticles or metal oxide nanoparticles, leading to
5 graphene coated metal nanoparticles.

[0097] After etching away the metal nanoparticles or metal oxide nanoparticles in acid, alkaline solution or other etchants, graphene-like carbon hollow structures or fullerenes are obtained. The as-obtained graphene-like carbon hollow structures or fullerenes (carbon nanoonions) contain monolayer or multilayer graphene. Other
10 supporting materials such as carbon nanotube, graphite, carbon nanofibers, graphene, activated carbon, carbon cloth and so forth can be used to support and disperse fullerenes, reducing the aggregation of fullerene nanoparticles.

[0098] In addition, during the growth of graphene-like carbon on the interface of metal or metal oxide and solid carbon, metal atoms can participate into the growth of
15 graphene and bond with C atoms of graphene, causing metal atoms doped-/bond with graphene crystals and leading to metal atoms doped- or surface-functionalized graphene-like shells after the etching process. Moreover, other atoms such as nitrogen, oxygen, sulfur, phosphorus, boron, hydrogen, fluorine, silicon, iodine, bromine from the solid carbon and metallic compounds can also dope in graphene
20 crystals during growth of graphene.

[0099] In addition, by partially and selective etching, residual metal or metal oxides nanoparticles can be left in the cavities enclosed by the shells. These residual metal or metal oxides nanoparticles can sever as catalyst nanoparticles. Furthermore, these residual metal or metal oxides nanoparticles can be used for synthesis of other
25 metallic compounds nanoparticles as catalyst nanoparticles by the chemical conversion approaches such as synthesis, chemical and electrochemical deposition, oxidation, reduction, thermal treatment, photochemical reaction, decomposition, replacement reaction, solid-state reactions, substitution, addition and elimination, complexation, carburizing, nitriding, chemical vapor deposition, etching, etc.

[00100] The C/S composites are then synthesized by using molten sulfur method, which is filling the liquid sulfur into the cavities of graphene-like carbon hollow structures such as fullerenes driven by capillary effect at a temperature from 100 °C to 600 °C for 0.1 hour to 48 hours. After cooling, the sulfur nanoparticles are solidified from liquid sulfur. The pathway for the diffusion of liquid sulfur is the holes in graphene
35 walls induced by the defects. The sulfur content can be adjustable from 50% to 98% by weight.

[00101] In addition, the composite structure of the S core-g-C₃N₄ shell can be also synthesized by the method including the abovementioned steps:

[00102] (1) First, uniformly mix one of the metal nanoparticles, metal hydroxides, and metal oxides nanoparticles with carbon precursors and electrically
5 conductive supporting materials in solution under stirring and/or ultrasonication at a temperature from -30°C to 350 °C. In fact, other non-porous metallic nanoparticles with size smaller than 30 nm can replace metal nanoparticles, metal hydroxides, and metal oxides nanoparticles for growth of g-C₃N₄. The metallic compounds
10 nanoparticles can be at least one of metal nitrides, metal carbides, metal sulfide, metal phosphide, metal hydroxide, metal selenide, metal telluride, metal boride and the heterostructures of two or more listed above. The nitrogen-rich carbon precursors can be at least one of dicyandiamide, melamine, urea, cyanamide, melam, melem and thiourea.

[00103] (2) Next, dry the mixture at a temperature and pressure to obtain a
15 composite of solid-carbon wrapped the one of metal, metal hydroxides and metal oxide nanoparticles, said composite dispersed by the conductive supporting materials.

[00104] (3) After drying, the obtained dried mixture is heat treated at the temperature from 200 °C to 900 °C under protection by inert gas of at least one of argon, nitrogen and kept for 0.1 h to 24 h. During heat treatment, g-C₃N₄ layers grow
20 on the surface of the metal, metal and metal oxide nanoparticles, and then coat the nanoparticles to form the layered shell.

[00105] (4) After etching away the metal or metallic compounds nanoparticles in acid, alkaline solution or other etchants, g-C₃N₄ hollow structures are obtained. The as-obtained g-C₃N₄ hollow structures contain a monolayer or multilayer shell. Other
25 supporting materials such as carbon nanotube, graphite, carbon nanofibers, graphene, activated carbon, carbon cloth and so forth can be used to support and disperse g-C₃N₄ hollow structures, reducing the aggregation of hollow structures.

[00106] In addition, the shell of hollow the g-C₃N₄ structures can be doped with foreign adatoms during growth of g-C₃N₄.

[00107] In addition, by partially and selective etching, residual metal and
30 metallic compounds nanoparticles can be left in the cavities enclosed by the shell of the composites. These residual metal and metallic compounds nanoparticles can sever as catalyst nanoparticles. In further, these residual metal and metallic compounds nanoparticles can be used for synthesis of other metallic compounds
35 nanoparticles as catalyst nanoparticles by the chemical conversion approaches such as synthesis, chemical and electrochemical deposition, oxidation, reduction, thermal

treatment, photochemical reaction, decomposition, replacement reaction, solid-state reactions, substitution, addition and elimination, complexation, carburizing, nitriding, chemical vapor deposition, etching, etc.

5 **[00108]** The g-C₃N₄/S composites are then synthesized by using the molten sulfur method. The pathway for the diffusion of liquid sulfur is the holes in g-C₃N₄ walls. The sulfur content can be adjustable from 50% to 98% by weight.

10 **[00109]** The above synthesized core-shell composite structure on the basis of graphene-like carbon shell and g-C₃N₄ shell can be used for the preparation of sulfur cathodes of metal-sulfur batteries such as lithium-sulfur batteries. Lithium-ion
15 batteries are the important renewable energy sources, which are widely used for various commercial applications such as portable electronics, electric vehicles, and the grid. However, the state-of-the-art lithium batteries still have many unresolved issues such as low energy density, high cost, and short life. Lithium-sulfur (Li-S) batteries represent a promising energy storage system with a superior theoretical
20 energy density of 2600 Wh/kg, up to a five-fold increase compared with the state-of-the-art Li-ion batteries. As an inexpensive and earth-abundant element, sulfur is endowed with a theoretical specific capacity of 1675 mAh/g and can be one of the most promising next generation cathode materials.

25 **[00110]** The current Li-S batteries are hindered by a number of problems: the low practical capacity, fast capacity fading, poor discharge and charge performances at high-current densities, as well as safety issues. These problems are mainly caused by the following reasons: (a) poor electrically and ionic conductivity of both sulfur and lithium sulfide (end product after fully discharge); (b) "shuttle effect" caused by high solubility of intermediate polysulfides (Li₂S_x, x=3-8) in the electrolyte. (c) a large
30 volumetric expansion of ~80% upon full lithiation to lithium sulfide, which can cause pulverization and structural damage at the electrode level, and (d) lithium dendrites formation. As a result, current lithium-sulfur batteries can only work well for a few hundred charging cycles. The above as-disclosed core-shell composite structure can be used for sulfur cathodes and effectively solve these problems to obtain high-performance metal-sulfur batteries.

35 **[00111]** The preparation of sulfur cathodes with using the as-disclosed core-shell composite structure may comprise the following steps:

(1) Prepare slurry by uniformly mixing the as-disclosed composite structure with electrical conductive additives and binders in a solvent;

(2) Cast the slurry onto current collectors such as Al;

(3) The sulfur cathodes are obtained after drying the current collectors coated with slurry and/or cutting in proper sizes, and then can be used for making metal-sulfur batteries.

[00112] The electrical conductive additives for slurry are used to improve the electrical conductivity of the electrodes, and can be at least one of carbon nanotube, graphite, carbon nanofibers, graphene, activated carbon, carbon cloth, carbon black and so forth. The weight content of the electrical conductive additives in the dried coating on the current collector is from 0 to 10%.

[00113] The binders can be at least one of polyvinylidene fluoride (PVDF), polyethylene oxide (PEG), poly(vinylpyrrolidone) (PVP), ethylene propylene diene monomer (EPDM) rubber, carboxymethyl cellulose (CMC), styrenebutadiene rubber (SBR), acrylonitrile multi-copolymer, polyvinyl alcohol (PVA), polyethylene oxide (PEO), poly(methyl methacrylate) (PMMA), polyacrylic acid, polyethyleneimine, β -Cyclodextrin, ammonium polyphosphate. The weight content of the binder in the dried coating on the current collector is from 0 to 10%.

[00114] The solvent for making the slurry can be at least one of water, N-methyl-2-pyrrolidone (NMP), ethanol, acetone, butanol, 2-ethoxyethanol, 1,4-dioxane, diethyl ether, tetrahydrofuran, dimethylformamide, acetonitrile, propylene carbonate, n-butanol, isopropyl alcohol, n-propanol, methanol, acetic acid, pyridine, ethylene glycol, triethylene glycol, diethyl ether, diethylene glycol, methyl t-butyl ether, nitromethane.

[00115] The current collector coated by the slurry can be at least one of the Al foil or foam, Ni foam, iron foam, carbon nanotube membrane, or carbon nanofiber membrane or porous graphene foam, graphene coated Al foil or foam, carbon coated Al foil or foam, porous carbon foams, other metal mesh networks or metal nanowire networks and so forth.

[00116] The loading of the sulfur on electrodes is from 0.5 to 100 mg/cm².

[00117] The metal-sulfur batteries consist of the above sulfur cathodes as positive electrodes.

[00118] The metal-sulfur batteries also consist of the negative electrodes. The active materials of the negative electrodes include at least one of the metals of Li, Mg, Al, Fe, Zn, Na, K, Ca, Ba, Cr. The negative electrodes can be pure metal foils of Li, Mg, Al, Fe, Zn, Na, K, Ca, Ba, Cr, or coatings, mixtures or composites containing active materials of the metals of Li, Mg, Al, Fe, Zn, Na, K, Ca, Ba, Cr. The negative electrodes may comprise a current collector made in forms of foils, foams or porous membranes of copper, iron, nickel, graphite, carbon black, carbon nanotube, amorphous carbon, carbon nanofibers, carbon nanobelts, graphene and the

combination of two or more of the list. The negative electrodes may also comprise binders such as at least one of polyvinylidene fluoride (PVDF), polyethylene oxide (PEG), poly(vinylpyrrolidone) (PVP), ethylene propylene diene monomer (EPDM) rubber, carboxymethyl cellulose (CMC), styrenebutadiene rubber (SBR), acrylonitrile multi-copolymer, polyvinyl alcohol (PVA), polyethylene oxide (PEO), poly(methyl methacrylate) (PMMA), polyacrylic acid, polyethyleneimine, β - cyclodextrin, ammonium polyphosphate. The ratio of the binder to the active materials is from 0 to 1:8. The negative electrodes may also comprise electrical conductive additives including at least one of carbon nanotube, graphite, carbon nanofibers, graphene, activated carbon, carbon cloth, carbon black and so forth. The ratio of the electrical conductive additives to the active materials is from 0 to 1:8.

[00119] The metal-sulfur batteries also consist of the separators, which can be but not limit to polypropylene (PP), polyethylene (PE), polyimide (PI).

[00120] The metal-sulfur batteries also consist of the electrolyte, which may contain the salts containing metallic cations of the same element with the active materials of the anode and anions at least one of ClO_4^- , PF_6^- , CF_3SO_3^- , AsF_6^- , $\text{N}(\text{CF}_3\text{SO}_2)_2^-$, $\text{B}(\text{C}_6\text{H}_5)_4^-$, BF_4^- , SCN^- , and so forth. The electrolyte can be a liquid containing solvents or in solid state that comprises ionically conductive solid-state materials.

[00121] Fig. 1-3 are a schematic showing the cross-sectional view of examples of the composite structures as described above; Fig. 1 schematically shows the cross-sectional view of the core-shell composite structure as described above; Fig. 2 schematically shows the cross-sectional view of the core-shell composite structure with catalysts embedded in the cavity enclosed by the shell as described above; Fig. 3 schematically shows the cross-sectional view of the core-shell composite structure with functionalized groups on internal surface of the shell as described above.

[00122] Fig.4 shows a schematic illustration of the synthesis of fullerenes or carbon onions-sulfur composites anchored on CNT networks in the assistance of Ni nanoparticles (NPs) and used for lithium-sulfur batteries as described above. The synthesis of defective fullerenes is by thermal conversion of solid-carbon to fullerene-like carbon or graphene-like carbon in the assistance of metal nanoparticles. The metal nanoparticles play functions both as catalysts and templates. As catalysts, they help the conversion of solid carbon to sp^2 carbon with graphitic structures. As templates, after etching the metal nanoparticles, cavities are left for hosting sulfur. Typically, there are the following steps for the synthesis of fullerene-based sulfur electrodes:

[00123] (i) Synthesis of nickel hydroxides nanoparticles. The nickel hydroxides nanoparticles are prepared based on the reaction between alkaline solution and nickel salts. Specifically, the nickel salts can be nickel nitrate, nickel chlorides, nickel sulfides, nickel acetates and so forth. The alkaline solution can be sodium hydroxides, potassium hydroxides, calcium hydroxides, ammonia. The particle size of nickel hydroxides is around 1 nm to 50 nm.

[00124] Except nickel hydroxides nanoparticles, NiO nanoparticles or Ni nanoparticles (such as sputtered Ni) with size of around 1 nm to 50 nm can also be used in this step and the following steps.

[00125] The abovementioned nanoparticles can be dried or kept in a liquid solvent such as water or stabilized with surfactants or organics.

[00126] In addition, other metals such as Zr, Nb, Mo, Tc, Rh, Pt, Ir, Os, Re, La, Hf, W, Ni, Cu, Fe, Co, Pt, Au, Ag, Ti, Zn, Ta, Mn, Cr, Sn, V, Cd, Ru, Pd, or their alloys, mixtures or compounds can be also used in this step and the following steps.

[00127] During this step, other supporting materials such as carbon nanotube, graphene, graphene oxides, reduced graphene oxides, carbon nanofibers, graphite, metal nanowires, and metal foam and so on can be added.

[00128] (ii) Synthesis of nickel hydroxides nanoparticles-polymer dispersion. The nickel hydroxides nanoparticles dispersed in a liquid such as water to form a dispersion. Then polymers such as Polyvinylpyrrolidone are added in the liquid such as water to form a new dispersion. Stirring and ultrasonication are required for achieving a good dispersion. After well dispersed, the mixture is dried under stirring to have solid carbon-nickel hydroxides nanoparticles composites.

[00129] During this step, other supporting materials such as carbon nanotube, graphene, graphene oxides, reduced graphene oxides, carbon nanofibers, graphite, metal nanowires, and metal foam and so on can be added.

[00130] (iii) Thermal treatment. The solid carbon-nickel hydroxides nanoparticles composites above are then heated at a temperature for a duration. The holding temperature is in the ranges 200-900 °C, preferably at 300-700 °C, more preferably at 400-600 °C,. The holding time is from 1 second to 24 hours and preferably from 0.5h to 10 h. The heating up rate is 1 °C/min to 500 °C/min and preferably 1 °C/min to 10 °C/min. The cooling rate is from 1 °C/min to 500 °C/min and preferably from 1 °C/min to 50 °C/min. The gases can be one of nitrogen, hydrogen, argon or their mixtures but not limited to any of them. The gas flow is from 1 ml/min to 1m³/min.

[00131] (iv) After thermal treatment, the product is etched in chemicals to remove the metal nanoparticles and then fullerenes (carbon nanooions) or fullerenes (carbon nanooions) on supporting materials. The etchant is depending on the metals used. Typically for Ni, Cu, Co, Fe and zinc nanoparticles, hydrochloride acid with a concentration from 0.1 M to 5 M or the FeCl₃ aqueous solution with a concertation from 0.1 M to 12 M can be used. The etching time can be 5 min to 24 h. After etching, fullerenes (carbon nanooions) or fullerenes (carbon nanooions) on supporting materials will be obtained.

[00132] It should be pointed out that, by controlling the solid carbon content in solid carbon-nickel hydroxides nanoparticles composites, the walls of fullerenes (carbon nanooions) can be adjusted from monolayer to multilayer. By controlling the type of solid carbon used, the carbon walls can be doped with heteroatoms such as oxygen, nitrogen, sulfur, boron, phosphorus, metals and so forth on the external of shells or internal surface of shells. By controlling the temperature and cooling rate, the wall thicknesses of fullerenes (carbon nanooions) can also be adjusted. By controlling the solid carbon and temperatures the graphitization and defects content can be tuned. By controlling the size of metallic nanoparticles and parameters of heating treatment (temperature, time, gases, cooling) the size of fullerenes (carbon nanooions) can be adjusted.

[00133] It should be also mentioned that, by controlling the etching and post functionalization, the surface can be functionalized such as contained functional groups of hydroxyl, carbonyl, aldehyde, haloformyl, carbonate ester, carboxylate, carboxyl, ester, methoxy, or nitrogen contained functional groups such as amide, amines, imine, nitrile, isonitrile, pyridyl, or sulfur contained functional groups such as sulfhydryl, sulfide, sulfinyl, or boron contained functional groups, or halogen contained functional groups.

[00134] It also should be pointed out that, by controlling the etching the metallic nanoparticles can be partially removed. The left metallic nanoparticles inside of cavities of fullerenes or carbon onions can be used for synthesis of metal oxides, metal nitrides, metal sulfides, metal phosphides, metal carbides, metal halide or other metal compounds. Besides, exotic metallic nanopariticles can also be synthesized after etching by chemical reaction in a liquid or a gas system.

[00135] (v) For the application of the as-prepared fullerenes or carbon onions for lithium-sulfur batteries, they can be as good host materials for sulfur cathodes by fill sulfur inside the cavities of fullerenes or carbon onions. This can be achieved by mixing the fullerenes or carbon onions with sulfur with a weight ratio in the range of

3:1 to 1:30 and heating them at a temperature of 100-600 °C, preferably at 155 °C. The mixture of fullerenes or carbon onions and sulfur can be obtained by physical mixing like mechanical milling or chemical mixing. Owing to the holes on walls of fullerenes or carbon onions, liquid sulfur molecular can enter the cavities of fullerenes or carbon onions and concrete to sulfur nanoparticles. The sulfur filled in the cavities of fullerenes or carbon onions achieves intimate contact with fullerene-like or graphene-like carbon. Importantly, the particle size of C-S composites is very small and can be controlled in the range of 1-30 nm.

[00136] After synthesis of fullerene-sulfur composites, the sulfur electrodes can be prepared by using casting method on Al foil. Typically, mix the fullerene-sulfur composites with binders such as polyvinylidene difluoride (PVDF) or polyvinylpyrrolidone (PVP) or carboxymethyl cellulose (CMC) or poly(3,4-ethylenedioxythiophene) (PEDOT) and conductivity additives such as Super P carbon black or carbon nanotube or carbon nanofibers in a liquid solvent such as N-Methyl-2-pyrrolidone (NMP) to make a slurry. Then use casting method (or other method such as rod coating, spraying coating, spinning coating) making slurry into a coating onto Al foil, followed with drying at temperature 20-90 °C under a pressure. After drying, the content of binder in the mixture can be 1-15 wt.%. The content of conductive additives in the slurry can be 1-25 wt.%. The drying pressure can be atmospheric pressure to 1×10^{-6} mbar.

[00137] The electrodes of fullerene-sulfur composites can be also binder-free and aluminum-free electrodes. Alternatively, the fullerene-sulfur composites can also be supported by carbon nanotube networks or carbon nanofiber networks or porous graphene foam or metal mesh networks or metal nanowire networks, or porous carbon foams and so forth. For example, pyrolyzed electrospun nanofibers are can be used as current collectors. The electrodes can be lighter than Al-based and binder-based electrodes. The sulfur loading can be higher. The gravimetric and volumetric capacity of electrodes can be higher than Al-based and binder-based electrodes.

[00138] Importantly, the electrodes of fullerene-sulfur composites can exhibit long-life and high capacities. Owing to the small size of sulfur nanoparticles and C-S particles, the utilization of sulfur can reach 100%. The rate-performances of the Me-S batteries such as Li-S batteries can be significantly improved. Owing to the physical and chemical confinement of sulfur inside the cavities of fullerenes or carbon onions, the dissolution and diffusion of polysulfides (S_x^{2-}) can be effectively restricted. Thus the life of batteries can be largely improved.

[00139] Fig. 5a shows the HRTEM image of $\text{Ni}(\text{OH})_2$ nanoparticles. As can be seen, the particle size is less than 20 nm. Fig. 5b shows the SEM image of composites of fullerene@Ni NPs after thermal treatment of $\text{Ni}(\text{OH})_2$ -PVP composites. The bright points are Ni nanoparticles, which have size less than 20 nm. Fig. 5c of TEM image of fullerene@Ni NPs clear demonstrates the Ni NPs. Fig. 5d of HRTEM image fullerene@Ni NPs clearly shows the Ni nanoparticles coated with graphitic carbon, which is fullerene-like carbon or graphene-like carbon. The size of the particles is ~10 nm. Fig. 5e shows the fullerene or carbon nanooxions after etching away the Ni nanoparticles. The fullerene or carbon nanooxions are highly aggregated together. Fig. 5f shows the HRTEM image of fullerene or carbon nanooxions. As can be seen, the cavities of fullerene or carbon nanooxions are 5-10 nm, and walls of fullerene or carbon nanooxions are multilayer. The thickness of walls is 1-3 nm.

[00140] Fig. 6a shows the HRTEM image of carbon nanotube supported fullerene spheres. As can be seen, the fullerene spheres are effectively dispersed by introducing CNT. The CNT is multilayer CNT as can be seen in Fig. 6b. The diameter of MWCNT is 10~15 nm and the thicknesses of walls is 2~4 nm. The size of cavities is ~5-9 nm. After etching, the CNT can open as seen in Fig. 6c. Except MWCNT, SWCNT or other carbon supporting materials such as carbon nanofibers can also be used. Fig. 6d shows a single-layer fullerene sphere anchored on MWCNT. Fig. 6e shows multilayer fullerene spheres anchored on CNT. The size of fullerene spheres is in the range of 3-15 nm.

[00141] The TEM image of fullerene@S NPs@CNT in Fig. 7a shows the microstructures of fullerene-sulfur composites. As can be seen, the sulfur nanoparticles marked with yellow arrows are embedded inside the fullerenes. The particle size is less than 20 nm, mostly is 5~10 nm. Fig. 7b-c clearly shows the sulfur nanoparticles are filled inside the cavities of fullerenes. Except, the sulfur can be also filled in the cavities of carbon nanotubes as shown in Fig. 7d. This can be selective and adjusted by controlling the opening of carbon nanotubes.

[00142] The electrochemical performances of fullerene-sulfur composites are very excellent. Fig. 8a shows the cyclic performances of fullerene@S NPs@CNT and a physical mixture of fullerene@S NPs and CNT with various content of CNT at 0.2 C (1C=1675 mA/g). The initial discharge and charge were performed at 0.05C. When CNT content is ~30 wt.%, the initial discharge capacity of fullerene@S NPs@CNT electrode reaches ~1620 mAh/g (based on sulfur), which is very close to the theoretical value of sulfur (1670 mAh/g) due to the unique structure of the core-shell composites. At 0.2C, the initial capacity could reaches 1200 mAh/g. After 100 cycles,

the capacity can still remain at 850 mAh/g. The capacity decay at 0.2C is 0.29% per cycle. The addition of CNT during the synthesis of fullerene and the content of CNT can influence the electrochemical performances of batteries. The fullerene@S NPs@CNT composites with content 10 wt.% CNT and 50 wt.% CNT have lower capacities because the content of CNT is out of the optimal range and influences the dispersivity and efficiency of fullerenes. A much lower initial capacity of around 966 mAh/g and fast capacity decay are measured for the physical mixture of fullerene@S NPs with 30% CNT, indicating the significance of introducing CNT during the synthesis production of materials to reduce the aggregation of fullerenes. Fig. 8b shows the cyclic performance of fullerene@S NPs@CNT (30 wt. %) at 5 C. It shows the fullerene-sulfur electrode has a long life that it can cycle for 2000 cycles. The initial capacity at 5C is 524 mAh/g. After 2000 cycles, the capacity can remain at 252 mAh/g. The capacity decay is only ~0.026% per cycle. It should be pointed out that, the performances of fullerene-sulfur electrode can be further improved by adjusting the walls thicknesses and defect content of fullerenes. According to an embodiment, the plurality of core-shell structures are dispersed with an average distance between the plurality of core-shell structures ranging from 0.04 nm to 150 nm, preferably from 0.04 to 50 nm, more preferably from 0.04 to 10 nm. The average distance is measured from shell to shell.

20 **[00143]** Fig. 9 schematically illustrates the charge and discharge processes of fullerene@S NPs composites. During discharge, the lithium ions diffuse into the cavities of fullerene via the holes and react with the sulfur. The electrons transport through the carbon nanotube and walls of fullerenes to sulfur. Owing to the small nanoparticles of sulfur, the sulfur has a high utilization, which helps the batteries achieved a high capacity. In addition, soluble polysulfides formed during discharge. But, due to the small holes of walls, the polysulfides cannot or severely diffuse out of the cavities. Thus the polysulfides are effectively confined inside the cavities of fullerenes. This aids the Li-S cells working for a long life.

30 **[00144]** Fig. 10 shows the fullerenes or carbon nanooonions can also embed with CeO₂ nanoparticles. The nanoparticles can be prepared by chemical synthesis. Except metal oxides, metal nitrides, metal sulfides, metal phosphides, metal carbides, metal halide or other metal compounds can also be synthesized in fullerenes. Typically, these metal based materials can be the oxides, nitrides, sulfides, phosphides, carbides, halide, hydroxides or their hybrids of Ni, Cu, Fe, Co, Zn, Ti, Zr, Nb, Mo, Tc, Rh, Pt, Ir, Os, Re, La, Hf, W, Pt, Au, Ag, Ta, Mn, Cr, Sn, V, Cd, Ru, Pd.

35 The functions of these nanoparticles include chemically interact with polysulfides and

affect the kinetics of phases transformation between lithium polysulfides and lithium sulfides.

[00145] In the foregoing description of the figures, the invention has been described with reference to specific embodiments thereof. It will, however, be evident
5 that various modifications and changes may be made thereto without departing from the scope of the invention as summarized in the attached claims.

[00146] In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to
10 the particular embodiments disclosed, but that the invention will include all embodiments falling within the scope of the appended claims.

[00147] In particular, combinations of specific features of various aspects of the invention may be made. An aspect of the invention may be further advantageously enhanced by adding a feature that was described in relation to another aspect of the
15 invention.

[00148] It is to be understood that the invention is limited by the annexed claims and its technical equivalents only. In this document and in its claims, the verb "to comprise" and its conjugations are used in their non-limiting sense to mean that items following the word are included, without excluding items not specifically mentioned. In
20 addition, reference to an element by the indefinite article "a" or "an" does not exclude the possibility that more than one of the element is present, unless the context clearly requires that there be one and only one of the elements. The indefinite article "a" or "an" thus usually means "at least one".

Claims

1. A composite structure, comprising:
an electrically conductive supporting material;
5 a plurality of core-shell structures, said core-shell structures comprising:
a shell comprising carbon;
a cavity enclosed by the shell;
a core in the cavity, said core comprising sulfur;
wherein the shell comprises a layered structure with pores connecting the cavity and
10 outside of the shell, said pores have an average size ranging from 0.2 nm to 5 nm,
preferably from 0.4 nm to 2 nm, more preferably from 0.4 nm to 1 nm,
wherein the plurality of core-shell structures are dispersed in the composite structure
by the conductive supporting material between the plurality of core-shell structures.
- 15 2. The composite structure of claim 1, wherein the plurality of core-shell structures are
dispersed with an average distance between the plurality of core-shell structures ranging
from 0.5 nm to 150 nm, preferably from 0.7 nm to 50 nm, more preferably from 1 nm to
10 nm.
- 20 3. The composite structure of one of claims 1-2, wherein the electrically conductive
supporting material comprises at least one of the following for reducing aggregation of
the core-shell structures: carbon nanotubes, graphene, thin graphite, carbon nanofibers,
reduced graphene oxides, graphene oxides, activated carbon, porous graphene, porous
carbon, porous metals, porous conductive polymers.
- 25 4. The composite structure of one of claims 1-3, wherein the cavity has an average size
ranging from 1 nm to 30 nm, preferably from 1 nm to 20 nm, more preferably from 1 nm
to 10 nm, wherein the shell has an average thickness ranging from 0.4 nm to 10 nm,
preferably from 0.4 nm to 3.5 nm, more preferably from 0.4 nm to 2 nm.
- 30 5. The composite structure of one of claims 1-4, wherein the cavity comprises an average
pore volume ranging from 1.0 to 25.0 cm³/g, and an average specific surface area
ranging from 200 to 3500 m²/g.
- 35 6. The composite structure of one of claims 1-5, wherein the core-shell structures
comprise a sulfur content ranging from 50 to 98 wt.%.

7. The composite structure of one of claims 1-6, wherein the shell is functionalized at an internal surface of the shell with at least one of the following:
oxygen contained functional group, nitrogen contained functional group, sulfur contained functional group, boron contained functional group, halogen contained functional group,
5 for trapping soluble and polar polysulfides and lowering activation barrier energy of oxidation of Li_2S and other non-lithium metal sulfides.
8. The composite structure of one of claims 1-7, wherein the shell encloses catalyst
10 nanoparticles, such as metal, metal oxides, metal nitrites, metal sulfides, metal carbides, metal hydroxides, alloys, for trapping soluble and polar polysulfides and lowering activation barrier energy of oxidation of Li_2S and other non-lithium metal sulfides.
9. An electrode comprising the composite structure of one of claims 1-8, wherein an
15 average area loading of sulfur ranging from 0.5 to 200 mg/cm^2 .
10. A metal-sulfur battery comprising the electrode according to claim 9.
11. A method for producing a composite structure for an electrode, comprising the steps
20 of:
dissolving carbon-based organics in a colloid of one of metal, metal hydroxides and metal oxide nanoparticles, and adding an electrically conductive supporting material to form a mixed colloid;
drying the mixed colloid to obtain a composite of solid-carbon wrapped the one of
25 metal, metal hydroxides and metal oxide nanoparticles, said composite dispersed by the conductive supporting material;
heat-treating the obtained composite at a temperature from 200 °C to 900 °C under inert gas protection to obtain graphene-like carbon or graphitic carbon nitride coated metal or metal oxide nanoparticles by catalytic conversion of the solid-carbon to
30 graphene-like carbon or graphitic carbon nitride;
removing the one of metal, metal hydroxides and oxide nanoparticles to obtain a plurality of shell structures, said plurality of shell structures are dispersed by the conductive supporting material, said shell structures comprise:
a shell comprising carbon;
35 a cavity enclosed by the shell;

wherein the shell comprises a layered structure with pores connecting the cavity and outside of the shell, said pores have an average size ranging from 0.2 nm to 5nm, preferably from 0.4 nm to 2 nm, more preferably from 0.4 nm to 1 nm;

5 encapsulating sulfur in the cavities as cores enclosed by the shells to obtain the composite structure, said cores comprising sulfur.

12. The method according to claim 11, wherein the carbon-based organics or/and the solid carbon comprises at least one of polyvinylpyrrolidone, polyvinyl alcohol, polyethylene oxide (PEO), polyoxyethylene, poly(methyl methacrylate), triethylene
10 glycol, hydrocarbon, sugar, sucrose, lignin, dicyandiamide, melamine, urea, proteins, nylon, rubber.

13. The method according to one of claims 11-12, further comprising synthesizing sulfur in the cavity by placing the plurality of shell structures with the
15 supporting material in liquid sulfur at a temperature ranging from 100 to 600 °C under an atmosphere comprising at least one of Argon and Nitrogen.

14. The method according to one of claims 11-13, further comprising functionalising by surface chemical modifications such as oxidation, reaction with
20 oxygen/nitrogen/sulfur/boron/halogen contained functional groups at an internal surface of the shell with at least one of the following: oxygen contained functional group, nitrogen contained functional group, sulfur contained functional group, boron contained functional group, halogen contained functional group, for trapping soluble and polar polysulfides and lowering activation barrier energy of oxidation of Li_2S and other non-lithium metal
25 sulfides.

15. The method according to one of claims 11-14, further comprising enclosing catalyst nanoparticles, such as metal, metal oxides, metal nitrites, metal sulfides, metal carbides, metal hydroxides, alloys, for trapping soluble and polar polysulfides and lowering
30 activation barrier energy oxidation of Li_2S and other non-lithium metal sulfides.

Fig. 1

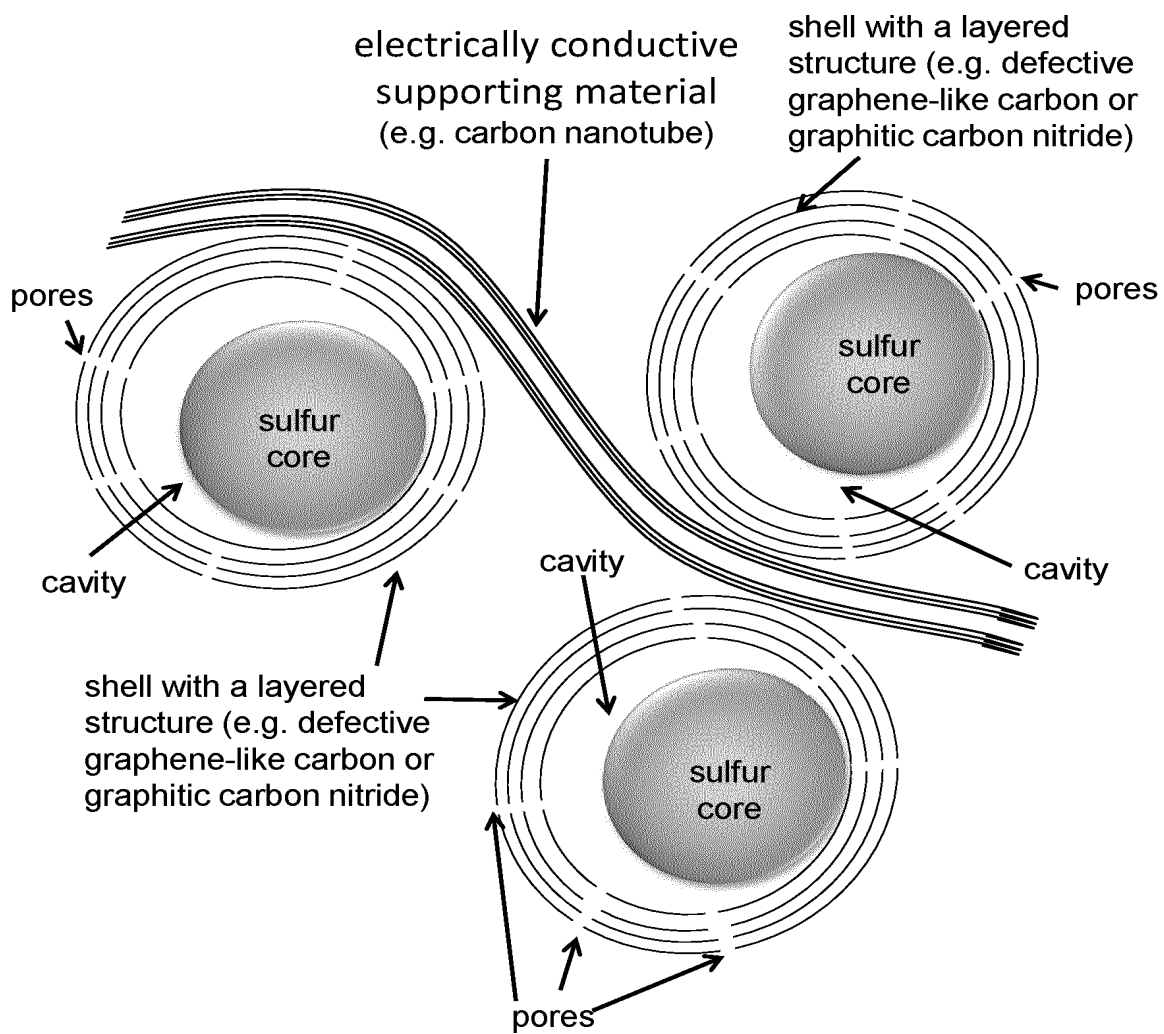


Fig. 2

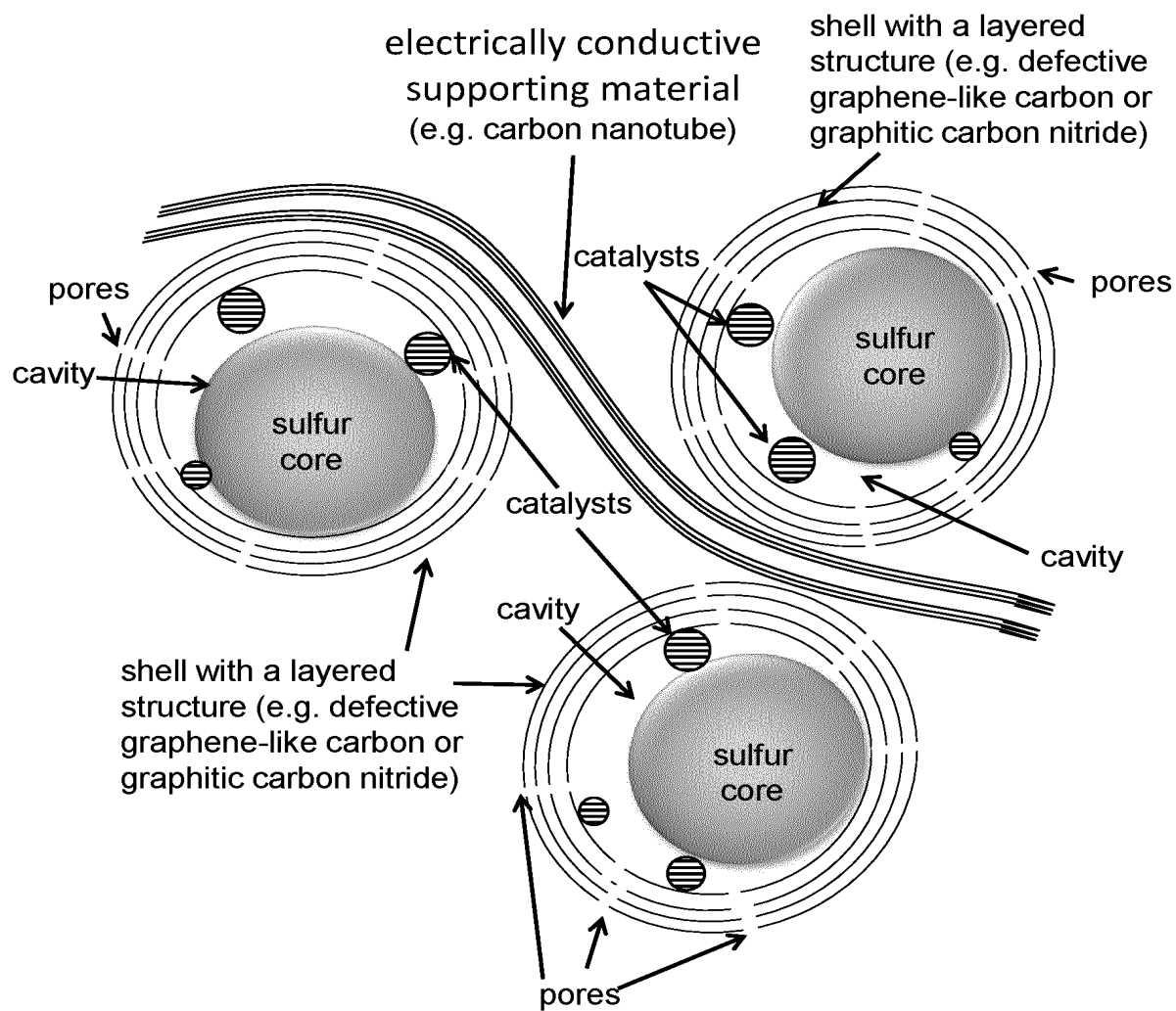


Fig. 3

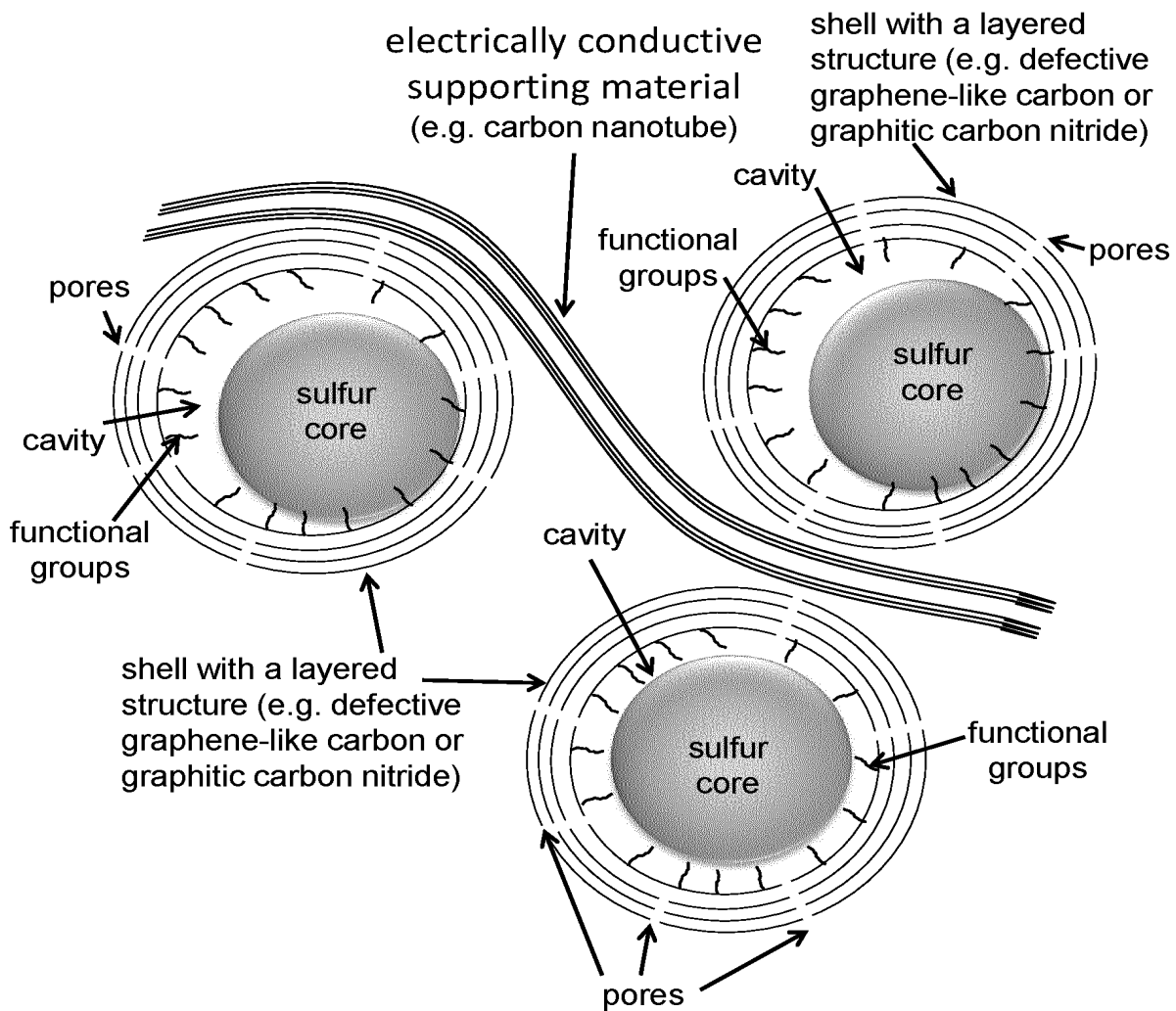


Fig. 4

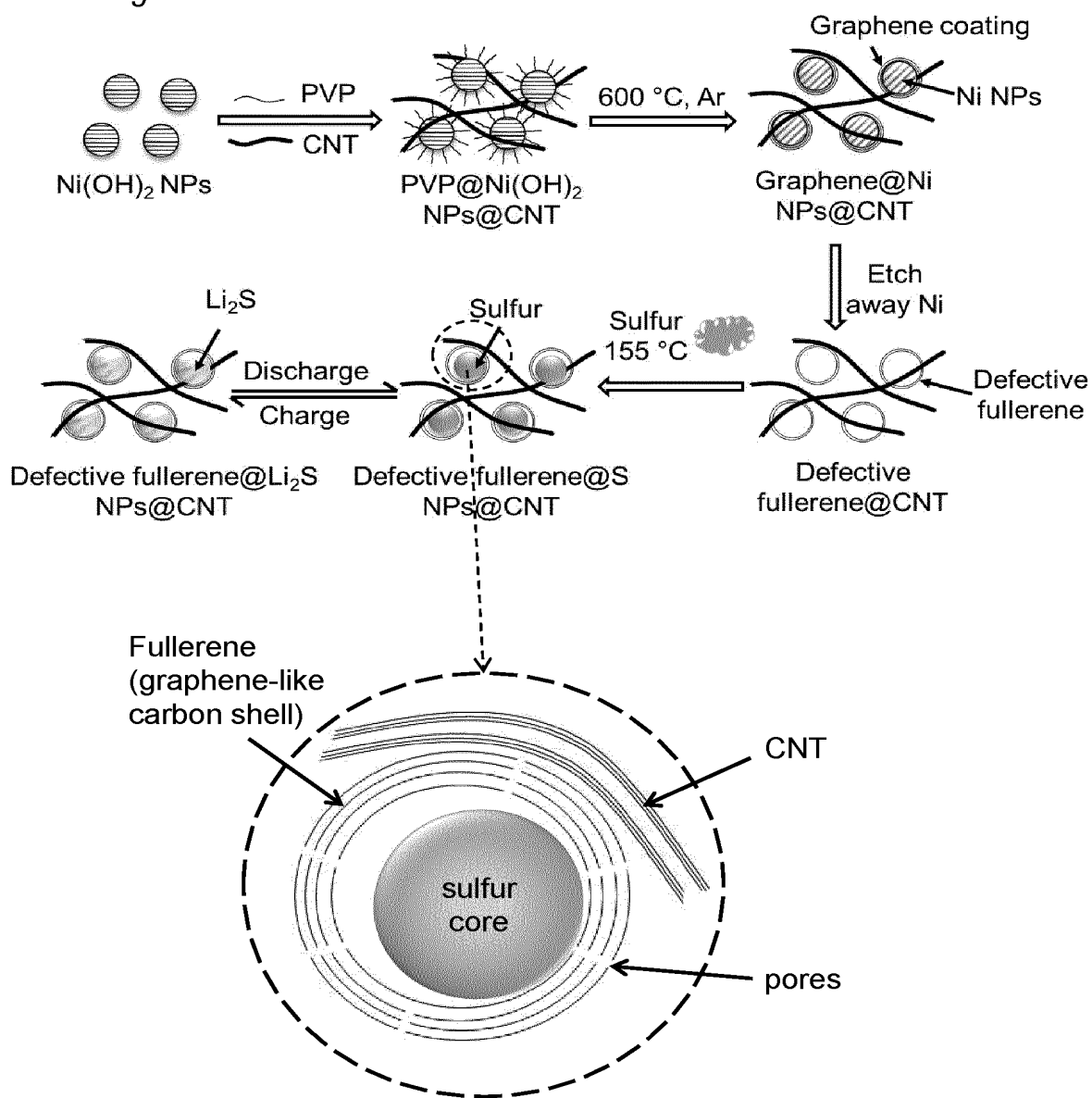


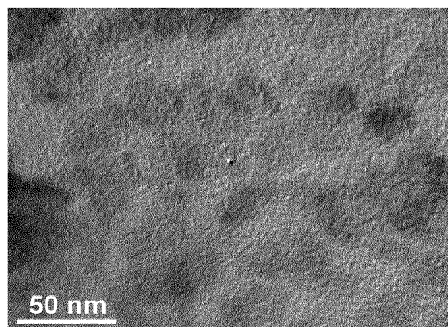
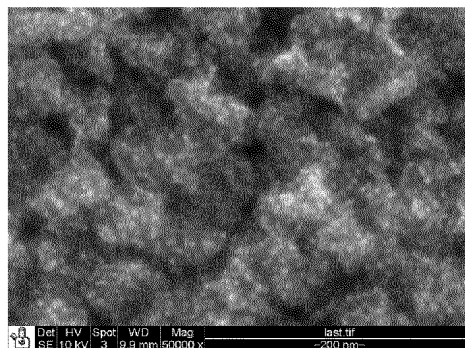
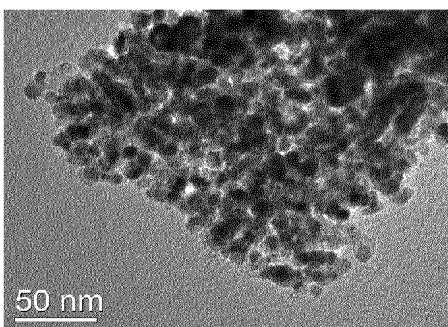
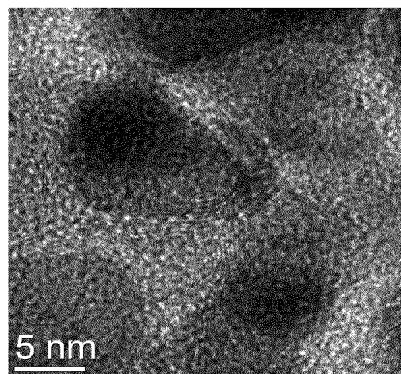
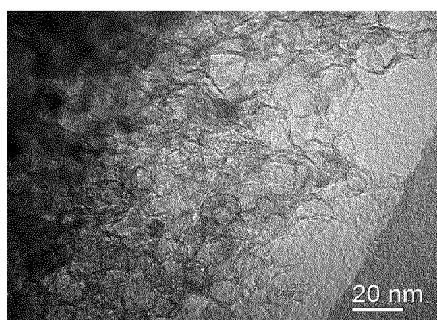
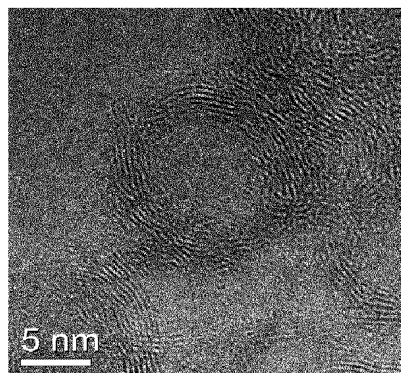
Fig. 5a*Fig. 5b**Fig. 5c**Fig. 5d**Fig. 5e**Fig. 5f*

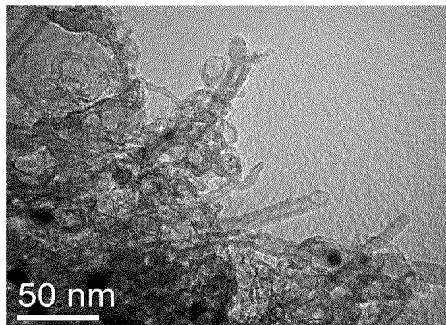
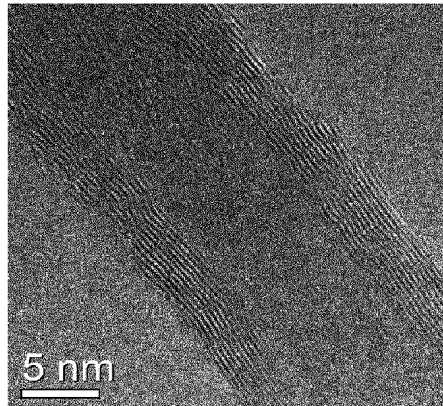
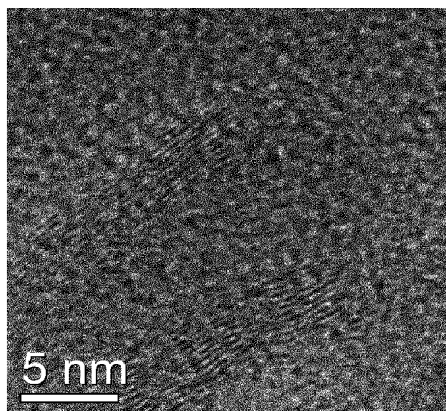
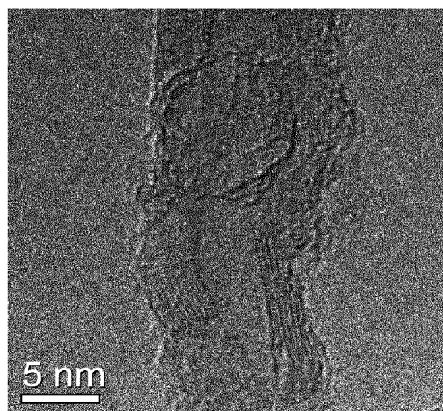
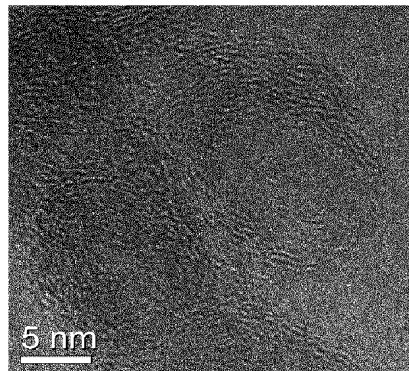
Fig. 6a*Fig. 6b**Fig. 6c**Fig. 6d**Fig. 6e*

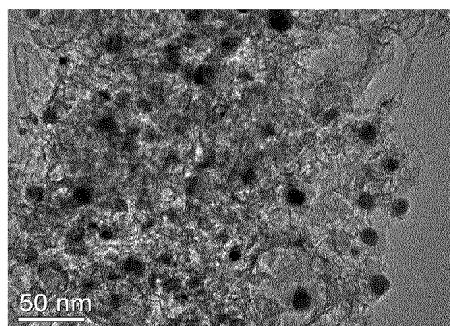
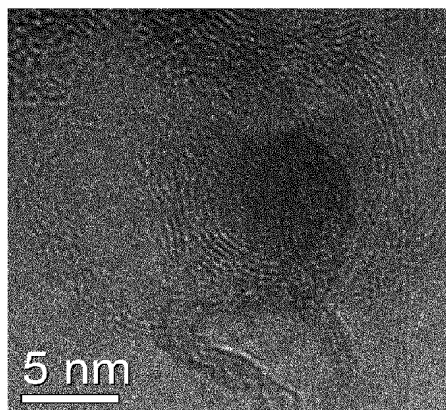
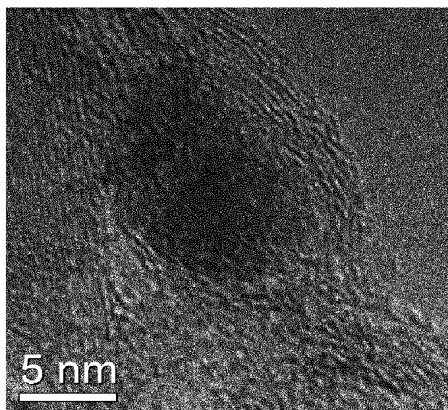
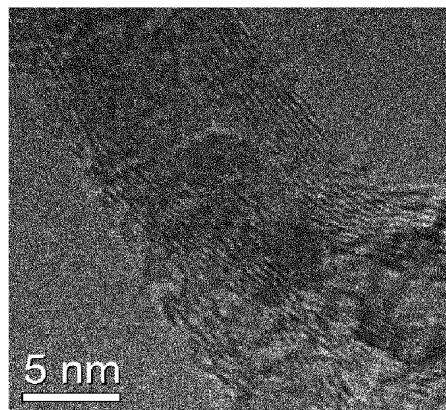
Fig. 7a*Fig. 7b**Fig. 7c**Fig. 7d*

Fig. 8a

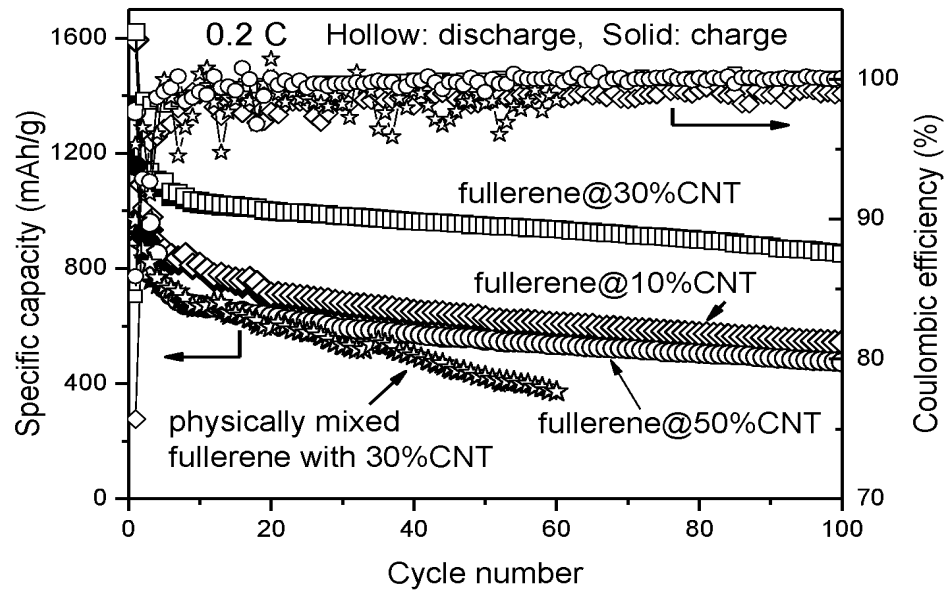


Fig. 8b

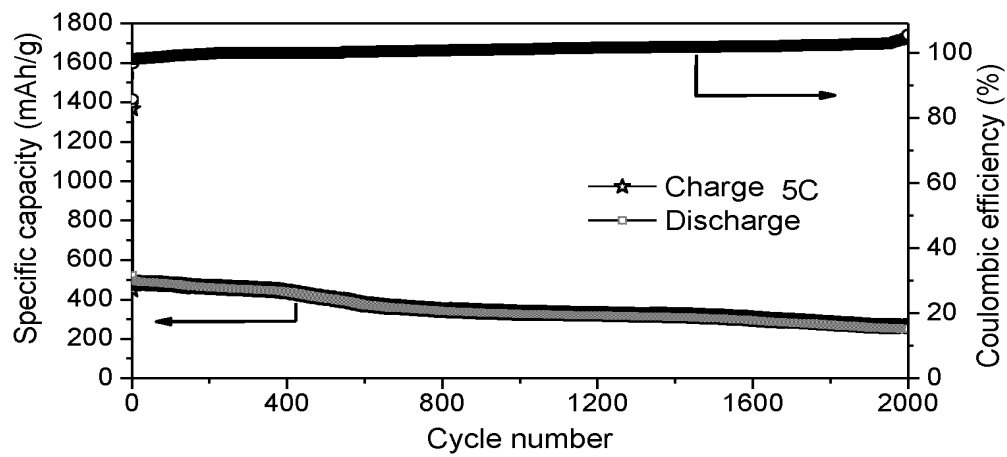


Fig. 9

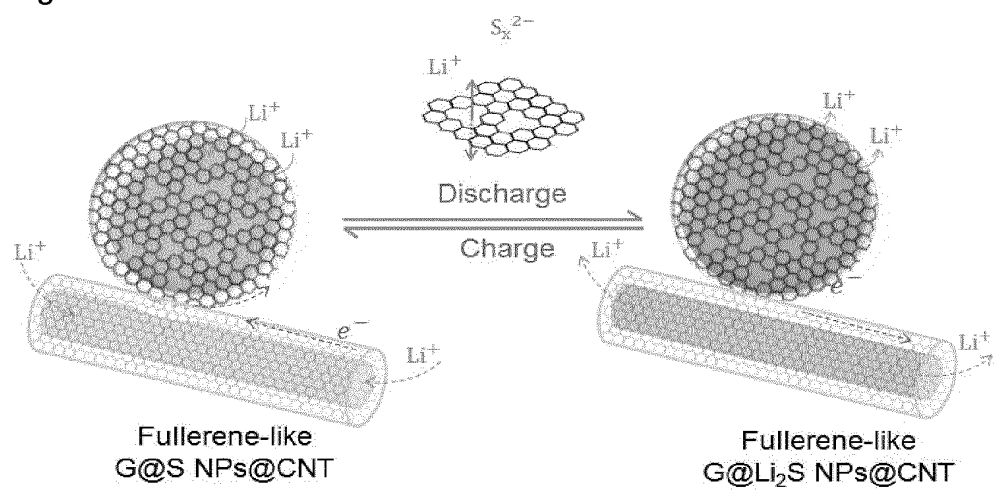


Fig. 10a

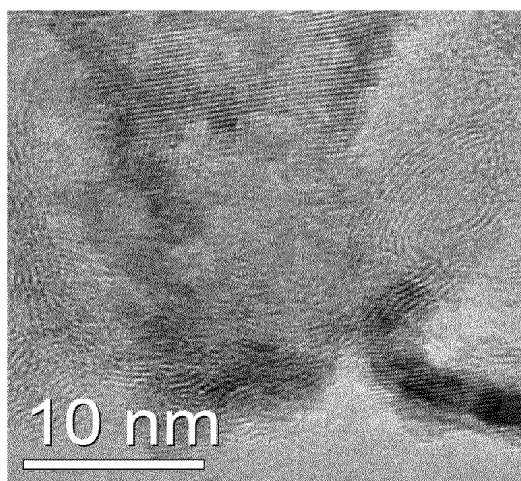
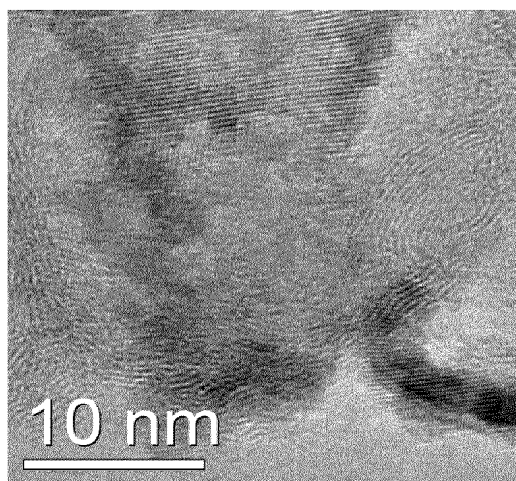


Fig. 10b



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2019/086987

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M4/137 H01M4/38 H01M4/38 H01M4/62
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2015/221935 A1 (ZHOU WEIDONG [US] ET AL) 6 August 2015 (2015-08-06) figures 1,2 paragraph [0018] - paragraph [0023] paragraph [0027] - paragraph [0032] paragraph [0036] - paragraph [0039] paragraph [0054] - paragraph [0055] claims 1-4 ----- - / - -	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

12 March 2020

Date of mailing of the international search report

20/03/2020

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/086987

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DELI WANG ET AL: "Infiltrating sulfur in hierarchical architecture MWCNT@meso C core-shell nanocomposites for lithium-sulfur batteries", PHYSICAL CHEMISTRY CHEMICAL PHYSICS, vol. 15, no. 23, 1 January 2013 (2013-01-01), page 9051, XP055559653, ISSN: 1463-9076, DOI: 10.1039/c3cp51551f page 9052 - page 9053 page 9054 - page 9055 -----	1-15
A	US 2016/087266 A1 (MULDOON JOHN G [US] ET AL) 24 March 2016 (2016-03-24) column 5, line 57 - column 6, line 44 column 8, line 28 - line 54 column 9, line 45 - column 10, line 11 example 2 -----	1-15
A	US 2018/219215 A1 (BUCUR CLAUDIU B [US] ET AL) 2 August 2018 (2018-08-02) paragraph [0016] - paragraph [0031] paragraph [0081] - paragraph [0083]; example 1 paragraph [0086] - paragraph [0094] -----	1-15
A	WO 2017/218150 A1 (UNIV TEXAS [US]) 21 December 2017 (2017-12-21) page 5, line 8 - page 6, line 23 page 14, line 31 - page 13, line 20 claims 1-38 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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